

**SYNTHESIS AND PROPERTIES  
OF 1-(5-NITRO-2-FURYL)-1-PHENYLSULFONYL-2-[5-(X-PHENYL)-  
-2-FURYL]ETHYLENES\***

A. JURÁŠEK, J. KOVÁČ and D. GEISBACHER

*Department of Organic Chemistry,  
Slovak Technical University, 880 37 Bratislava*

Received June 28th, 1973

Condensation of 5-nitrofurfuryl phenyl sulfone (*I*) with substituted 5-(X-phenyl)-2-furaldehydes (*II*) afforded the corresponding 1-(5-nitro-2-furyl)-1-phenylsulfonyl-2-[5-(X-phenyl-2-furyl)]-ethylenes *III* wherein X = H, 4-CH<sub>3</sub>, 4-OCH<sub>3</sub>, 4-NHCOCH<sub>3</sub>, 4-NH<sub>2</sub>, 4-NCS, 4-Cl, 4-Br, 4-COOH, 4-COOC<sub>2</sub>H<sub>5</sub>, 4-NO<sub>2</sub>, 3-NO<sub>2</sub>. The condensation mechanism was discussed on the basis of structures determined by means of UV and IR spectra, with respect to the possibility of the formation of isomers (isolated in some cases). The preparation of 5-(4-X-phenyl)-2-furaldehydes (X = COOC<sub>2</sub>H<sub>5</sub> and NHCOCH<sub>3</sub>) and 1(5-nitro-2-furyl)-2-(5-phenyl-2-furyl)ethylene is reported.

In an earlier paper<sup>1</sup>, an advantageous procedure has been reported for the preparation of saturated sulfones of the 5-nitrofuran series where the —CH<sub>2</sub>—group is located between the 5-nitrofuryl residue and the SO<sub>2</sub> group. The hydrogen atoms of the —CH<sub>2</sub>—group in these sulfones are acidified enough to effect an one-step preparation of 1,1,2-trisubstituted ethylene derivatives by condensation with carbonyl compounds. As indicated by UV spectra and inspection of models, these derivatives are not planar because of steric hindrance due to bulky substituents at the ethylene carbon atoms<sup>2</sup>.

In the present paper, we wish to report a procedure for the preparation of compounds *III* consisting in condensation of the sulfone *I* with substituted phenylfuraldehydes *II*. All the compounds *III* were prepared by a direct condensation except for the derivatives carrying a NH<sub>2</sub> and NCS group. The latter derivatives were obtained from the acetyl amino derivative *VII* by hydrolysis to give compound *VIII* and the subsequent treatment with thiophosgene. There is also reported the preparation of 5-(4-acetylaminophenyl)- and 5-(ethoxycarbonylphenyl)-2-furaldehydes by arylation of 2-furaldehyde with the corresponding diazonium salts as well as the synthesis of 1-(5-nitro-2-furyl)-2-(5-phenyl-2-furyl)ethylene (*XVI*) which was effected by the Wittig reaction of 5-nitrofurfuryltriphenylphosphonium bromide with 5-phenyl-

\* Part LI in the series Furan Derivatives; Part L: This Journal 39, 949 (1974).

2-furaldehyde. Compound *XVI* was used as a standard in evaluations of UV spectra.

Condensations of the sulfone *I* with arylfuraldehydes *II* was accomplished in glacial acetic acid under the catalytic action of ammonium acetate and piperidine at 110 to 115°C. The thus-obtained compounds and their properties are shown in Table I. The present yields are higher than in condensations of *I* with the corresponding aldehydes of the benzene series<sup>2</sup>. Compounds *III* are very sparingly soluble in polar as well as nonpolar solvents and are red to purple except for the derivative *XV* which is yellow.

TABLE I

Physical Properties and Elemental Analyses of 1-(5-Nitro-2-furyl)-1-phenylsulfonyl-2-[5-(X-phenyl)-2-furyl]ethylenes

Compound X	M.p., °C (yield, %)	Formula mol.w.	Calculated/Found			
			% C	% H	% N	% S
<i>IV</i>	185—186	C <sub>22</sub> H <sub>15</sub> NO <sub>6</sub> S	62.70	3.56	3.33	7.60
H	(41)	(421.4)	62.57	3.44	3.35	7.55
<i>V</i>	174—197	C <sub>23</sub> H <sub>17</sub> NO <sub>6</sub> S	63.40	3.93	3.22	7.35
4-CH <sub>3</sub>	(53.5)	(435.4)	63.20	3.73	3.35	7.33
<i>VI</i>	204—210	C <sub>23</sub> H <sub>17</sub> NO <sub>7</sub> S	61.22	3.79	3.10	7.10
4-OCH <sub>3</sub>	(59)	(451.2)	61.10	3.81	3.18	7.04
<i>VII</i>	135—138	C <sub>24</sub> H <sub>18</sub> N <sub>2</sub> O <sub>7</sub> S	60.24	3.79	5.85	6.68
4-NHAc	(52)	(478.4)	60.32	3.85	5.80	6.74
<i>VIII</i>	155—160	C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>6</sub> S	60.51	3.69	6.44	7.35
4-NH <sub>2</sub>	(32)	(436.4)	60.45	3.53	6.32	7.55
<i>IX</i>	170—174	C <sub>23</sub> H <sub>14</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub>	57.72	3.09	5.85	13.40
4-NCS	(46)	(478.5)	57.89	3.15	5.95	13.52
<i>X</i>	219—220	C <sub>22</sub> H <sub>14</sub> ClNO <sub>6</sub> S	57.96	3.09	3.07	7.03
4-Cl	(82.5)	(455.8)	58.07	3.01	3.12	7.11
<i>XI</i>	205—206	C <sub>22</sub> H <sub>14</sub> BrNO <sub>6</sub> S	52.81	2.82	2.80	6.40
4-Br	(83.5)	(500.3)	52.96	2.97	2.98	6.41
<i>XII</i>	245—250	C <sub>23</sub> H <sub>15</sub> NO <sub>8</sub> S	59.4	3.24	3.01	6.88
4-COOH	(60)	(465.4)	59.43	3.30	3.16	6.95
<i>XIII</i>	154—160	C <sub>25</sub> H <sub>19</sub> NO <sub>8</sub> S	60.85	3.88	2.84	6.50
4-COOC <sub>2</sub> H <sub>5</sub>	(78)	(493.5)	60.44	4.02	3.06	6.53
<i>XIV</i>	214—216	C <sub>22</sub> H <sub>14</sub> N <sub>2</sub> O <sub>8</sub> S	56.75	3.02	6.02	6.86
4-NO <sub>2</sub>	(57.5)	(466.4)	56.51	2.79	6.17	6.87
<i>XV</i>	220—224	C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>8</sub> S	56.75	3.02	6.02	6.86
3-NO <sub>2</sub>	(63)	(466.4)	56.94	3.17	6.04	6.85

TABLE II  
The UV and IR Spectral Data of 1-(5-Nitro-2-furyl)-1-phenyl-sulfonyl-2-[5-(X-phenyl)-2-furyl]ethylenes

Comp.	X	$\lambda_{\max}$ , nm (log $\epsilon$ ) <sup>a</sup>	$\tilde{\nu}(\text{NO}_2)$ as $\tilde{\nu}(\text{NO}_2)$ s	$\tilde{\nu}(\text{SO}_2)$ as $\tilde{\nu}(\text{SO}_2)$ s
IV	H	208 (4.35) i 224 (4.32) 234 (4.33) i 256 (4.21) 327 (4.36) i 391 (4.18)	1 490	1 352 1 323 1 152 1 378
V	4-CH <sub>3</sub>	208 (4.40) 223 (4.31) 236 (4.34) i 259 (4.27) 331 (4.35) i 402 (4.21)	1 498	1 352 1 322 1 150 1 378
VI	4-OCH <sub>3</sub>	208 (4.39) — 238 (4.30) 270 (4.29) i 332 (4.28) i 391 (4.24)	1 498	1 352 1 321 1 150 1 378
VII	5-NHAc	208 (4.72) i 218 (4.65) — i 266 (4.45) 324 (4.60) sh 413 (4.36)	1 505	1 352 1 329 1 151 1 378
VIII	4-NH <sub>2</sub>	207 (4.87) i 222 (4.70) i 239 (4.57) 282 (4.64) 313 (4.65) 412 (4.54)	1 506	1 353 1 328 1 152 1 379
IX	4-NCS	208 (4.39) i 220 (4.30) — i 280 (4.15) 338 (4.27) sh 407 (4.00)	1 502	1 353 1 328 1 152 1 380
X	4-Cl	207 (4.37) — 237 (4.34) i 258 (4.28) 329 (4.40) sh 391 (4.24)	1 488	1 352 1 321 1 150 1 378
XI	4-Br	208 (4.44) — 236 (4.36) 262 (4.33) 331 (4.44) sh 392 (4.28)	1 486	1 352 1 323 1 151 1 379
XII	4-COOH	208 (4.54) i 219 (4.49) — i 267 (4.19) 322 (4.43) 394 (4.13)	1 507	1 356 1 330 1 156 1 383
XIII	4-COOC <sub>2</sub> H <sub>5</sub>	208 (4.62) — i 238 (4.48) i 263 (4.42) 325 (4.62) 392 (4.45)	1 500	1 353 1 326 1 151 1 372
XIV	4-NO <sub>2</sub>	208 (4.31) i 221 (4.24) i 233 (4.24) — 325 (4.34) 407 (4.26)	1 520	1 352 1 322 1 152 1 379
XV	3-NO <sub>2</sub>	i 210 (4.35) — 231 (4.40) i 279 (4.14) 322 (4.39) 370 (4.18)	1 518	1 352 1 324 1 152 1 379

<sup>a</sup> i, inflex; sh, shoulder; the UV spectrum of the standard XVI: 207 (4.60), 241 (4.67), 330 (4.54), 448 (4.83).

The UV spectra of compounds *III* (Table II) exhibit several absorption bands in the region of  $\sim 210$  nm,  $\sim 220$  nm (in the form of inflex) (this band is absent with some compounds), 231–241 nm, and 322–338 nm, and an absorption band reaching to the visible region at 370–417 nm. The absorption bands from 210 to  $\sim 338$  nm may be ascribed to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  electron transitions localised in the 5-nitro-furan or arylfuran portion of the molecule<sup>3-5</sup>. The UV spectra of compounds *III* and model compounds suggest the nonplanarity (similar to 1-(5-nitro-2-furyl)-1-phenylsulfonyl-2-(2-phenyl)ethylenes<sup>2</sup>), particularly the weak K-band (370–417 nm) which frequently occurs in the form of a shoulder or inflex only. In the parent derivative *IV*, this band is shifted by 57 nm with respect to the standard compound *XVI* which is planar and exhibits a very strong K-band at 448 nm ( $\log \epsilon$  4.83). With the

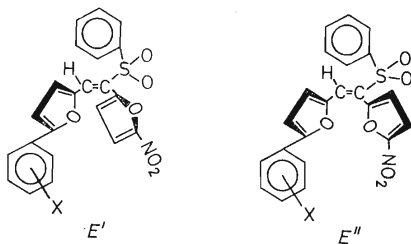


FIG. 1  
Conformation of *E* Isomers

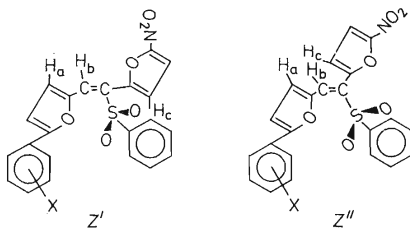


FIG. 2  
Conformation of *Z* Isomers

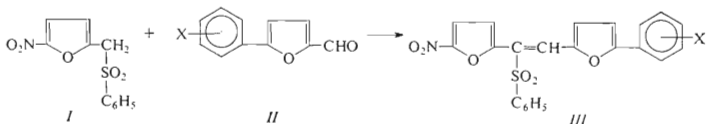
analogous compounds of the benzene series<sup>2</sup>, this shift is more distinct and represents the value of up to 116 nm in comparison with the corresponding standard. Also in the present case, the hypsochromic shift of the K-band is due to the twist of the 5-nitrofuranyl phenylsulfonyl and arylfuran residue from the plane of the ethylene molecule owing to the bulkiness of substituents. The resulting interruption of conjugation is then reflected in position and intensity of the K-band.

Figs 1 and 2 show the theoretically possible conformations of compounds *III*, inferred from models. In the case of conformers *E*, the nonplanarity of rings and the sterical hindrance is more evident than in the case *Z*. The furan rings are in conformers *E* oriented almost perpendicular to the plane of ethylene. Consequently, the mutual conjugation of furan rings does not exist at all or to an insignificant extent only. The substituted phenyl residue of the arylfuran moiety as well as the phenyl of the SO<sub>2</sub> group exhibit the free rotation. Depending on the conformation of furan rings, two conformers *E'* and *E''* may be formed. In the conformer *E'*, one furan ring is oriented by its oxygen atom under the plane and the other ring above the plane, while in the conformer *E''*, both the rings are simultaneously oriented under or above the plane of ethylene (Fig. 1). The conformation *Z* (Fig. 2) is energetically more advantageous since the system may assume such a structure which is more similar to the planar arrangement than in the case *E*. Notwithstanding, a complete coplanarity of both rings is impossible. In the case of the coplanar arrangement, oxygen atoms of arylfuran and the SO<sub>2</sub> group would come close together and would repulse themselves. Furthermore, the free rotation of the 5-nitrofuranyl and the arylfuran residue is not possible since the H<sub>c</sub> hydrogen and the 5-nitrofuranyl oxygen as well as the H<sub>a</sub> hydrogen of arylfuran interfere with the bulky SO<sub>2</sub> group. The H<sub>c</sub> hydrogen also interferes with the H<sub>b</sub> hydrogen of ethylene. From the two principal conformers *Z'* and *Z''*, the *Z'* one appears more advantageous since only one furan ring is oriented by its ring oxygen to the SO<sub>2</sub> group. The intensive colour of compounds *III* should suggest one of the conformations *Z*. The very weak and the strongly hypsochromically shifted (by 35–78 nm with respect to the standard) K-band is, however, at variance with such

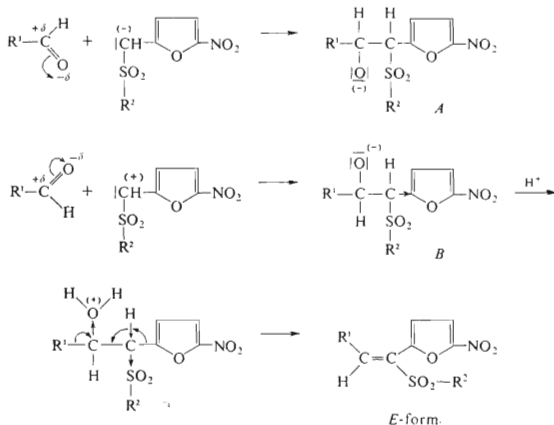
TABLE III  
Separation of Isomers

Compound	X	M.p., °C	Yields, %
<i>V</i>	4-CH <sub>3</sub>	174–175 and 195–197	14.3 and 85.7
<i>VI</i>	4-OCH <sub>3</sub>	204–205 and 209–210	5.7 and 94.3
<i>XIII</i>	4-COOC <sub>2</sub> H <sub>5</sub>	154–155 and 158–160	15 and 85

an idea. Most probably, compounds *III* as well as some other 1,1,2-trisubstituted ethylenes (unsaturated sulfones<sup>2</sup>) exist in the conformation *E* which (though less favourable from the steric standpoint than the arrangement *Z*) can be inferred from the probable mechanism of the condensation. In principle, there is necessary to take into account the stage of nucleophilic addition of the bulky carbanion to the carbonyl carbon atom or the transition states (*A*, *B*) of this reaction. It may be seen from Scheme 2 that the transition state *B* is much more advantageous than *A* since the negatively



SCHEME 1



SCHEME 2

$\text{R}^2 =$  aldehyde residue,  $\text{R}^1 = \text{C}_6\text{H}_5$

charged oxygen in near to the bulky  $\text{SO}_2$  group with two negatively charged oxygens in the case *A*, while in the *B* the more distant *anti*-periplanar position is assumed. Consequently, repulsions assert themselves in *B* to a much lesser extent than in *A*. After acceptance of two protons from the reaction medium, transition state *B* elimina-

tes water under the simultaneous removal of the strongly acidic hydrogen atom in *cis* position with respect to the eliminating OH group, the vacant atomic orbitals being replaced by the corresponding groups R and 5-O<sub>2</sub>NC<sub>4</sub>H<sub>2</sub>. Owing to steric factors, a special case of the *cis*-ionic elimination may be assumed leading to products of the configuration *E*. The colour of compounds *III* is probably due to the formation of strongly polar to quinonoid structures owing to the strong electron-accepting nature of the 5-nitrofuryl and phenylsulfonyl residues<sup>2</sup>. In accordance with this assumption, the 4-amino derivative *VIII* is more intensively coloured than the 3-nitro arylfuran derivative *XV* which is yellow.

In contrast to the substances reported in the earlier paper<sup>2</sup>, the present compounds do not exhibit sharp melting points (Table I). In some cases (compound *V*), the melting point range is as wide as 20°C. Some mixtures (Table III) were separated by fractional crystallisation or by chromatography on florisil<sup>6</sup>.

Table II shows characteristic infrared frequencies of compounds *III*. The  $\tilde{\nu}(\text{SO}_2)_s$  and  $\tilde{\nu}(\text{SO}_2)_{as}$  frequencies occur in the 1155–1150 cm<sup>-1</sup> and 1330–1321 cm<sup>-1</sup>, region, resp. These absorption bands are only to a low extent affected by the nature of the substituent. In all the present compounds, the  $\tilde{\nu}(\text{NO}_2)_s$  frequencies are split into two bands of a very strong and medium intensity at  $\sim 1550$  cm<sup>-1</sup> and  $\sim 1580$  cm<sup>-1</sup>, resp., analogously to the benzene series<sup>2</sup>, and also are little affected by the nature of the substituent. This influence is more significant with the  $\tilde{\nu}(\text{NO}_2)_{as}$  values. These

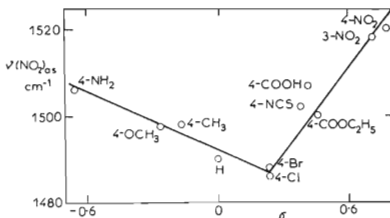


FIG. 3

Dependence of the Hammett  $\sigma$  Substituent Constants on the  $\tilde{\nu}(\text{NO}_2)_{as}$  Values

frequencies are shifted to lower values in comparison not only with other derivatives of the 5-nitrofuran series<sup>7</sup> but also with analogous unsaturated sulfones bearing a substituted aryl residue<sup>2</sup> instead of the arylfuran moiety. By plotting  $\tilde{\nu}(\text{NO}_2)_a$  versus the Hammett  $\sigma$  substituent constants, there are obtained two lines intersecting at the value corresponding to Cl and Br atoms. Two regression lines were computed (Fig. 3) for activation substituents ( $\rho = -21.64$ ;  $r = 0.99$ ) as well as deactivation substituents ( $\rho = 60.24$ ;  $r = 0.98$ ). The points for halo substituents were included in both correlations ( $\rho < 0$  and  $\rho > 0$ ).

## EXPERIMENTAL

## 5-(4-Acetamidophenyl)-2-furaldehyde

4-Aminoacetanilide (150 g; 1 mol) is added portionwise into a mixture of water (2 l) and 96% sulfuric acid (121 g; 1.2 mol). The mixture becomes thick during the sulfate formation. By cooling, the reaction mixture temperature is maintained at 10–15°C and a solution of sodium nitrite (70.6 g; 1.02 mol) in water (400 ml) is added dropwise over 1 h. The mixture is stirred at the same temperature for additional 1 h and then neutralised with 15% aqueous sodium hydrogen carbonate (131 g; 0.19 mol) to Congo Red paper. The thus-obtained solution of *p*-acetamidobenzene-diazonium sulfate is treated with furfural (123 g; 1.28 mol) in water (400 ml). The temperature is raised to 20–25°C and cupric chloride dihydrate (46 g; 0.27 mol) in water (200 ml) is added. The whole mixture is stirred at 40–50°C for 4 h and then kept at room temperature for 16 h. Crystallisation from ethyl acetate (ethanol) affords 44 g (19.2%) of the title compound, m.p. 185–188°C. For  $C_{13}H_{11}NO_3$  (229.2) calculated: 67.24% C, 4.83% H, 6.11% N; found: 67.03% C, 4.76% H, 6.23% N.

## 5-(4-Ethoxycarbonylphenyl)-2-furaldehyde

To a solution of ethyl 4-aminobenzoate (41.3 g; 0.25 mol) in 10% aqueous hydrochloric acid (150 ml) there is added dropwise at the temperature up to 5°C a solution of sodium nitrite (18 g; 0.26 mol) in water (50 ml), followed by furfural (26 g; 0.26 mol) and (at 30°C) cupric chloride dihydrate (11 g; 0.064 mol). The mixture is stirred at 30°C for 4 h and then kept at room temperature for 6 h. The crude product is collected with suction, washed with water, and recrystallised from ethyl acetate to afford 9 g (15%) of the title aldehyde, m.p. 115–116°C. For  $C_{14}H_{12}O_4$  (244.3) calculated: 68.82% C, 4.95% H; found 68.57% C, 5.02% H.

## 1-(5-Nitro-2-furyl)-2-(5-phenyl-2-furyl)ethylene

A mixture of triphenylphosphine (1.3 g; 0.005 mol), 5-nitrofurfuryl bromide (1 g; 0.005 mol), and benzene is refluxed for 3 h. After about 20 min, the solution begins to deposit a white precipitate of the complex salt which darkens in the course of the reaction. The mixture is allowed to stand overnight and the salt is collected with suction. Recrystallisation from the chloroform–light petroleum solvent mixture affords 1.7 g (73%) of 5-nitrofurfuryltriphenylphosphonium bromide. A mixture of this bromide (0.94 g; 0.002 mol), 5-phenyl-2-furaldehyde (0.35 g; 0.002 mol), water (20 ml), and 0.1M-NaOH (10 ml) is kept at room temperature for 24 h. The product is extracted into ether and purified by a repeated chromatography on a column (20 cm; 2 cm in diameter) of alumina (Brockmann activity II). Yield, 0.25 g (50%) of the title ethylene derivative; red crystals m.p. 136–140°C. For  $C_{16}H_{11}NO_4$  (281.2) calculated: 68.13% C, 4.96% H; found: 68.20% C, 4.89% H.

## Preparation of Compounds III

A stirred mixture of the sulfone *I* (2.67 g; 0.01 mol), ammonium acetate (1.54 g; 0.02 mol), the appropriate aldehyde *II* (0.01 mol), piperidine (1 ml), and acetic acid (25 ml) is heated at 110 to 115°C for 3 h. In the course of the reaction, crystals are deposited. The reaction mixture is poured onto ice (100 g) and the solid is collected with suction, washed with water, and purified by crystallisation or chromatography on alumina (Brockmann activity II; column length 20 cm, diameter 2 cm). Compounds *IV* and *V* were separated by fractional crystallisation from dioxane. Com-



pound XIII was purified by column (20 cm; 2 cm in diameter) chromatography on florisil (100 to 200 mesh) in the solvent system ether-n-hexane and crystallisation from dioxane.

1-(5-Nitro-2-furyl)-1-phenylsulfonyl-2-[5-(4-aminophenyl)-2-furyl]ethylene

The acetyl derivative VII (2.4 g; 0.005 mol) is refluxed in dilute (1 : 1) hydrochloric acid (50 ml) for 1 h. After cooling down, the amine hydrochloride is collected with suction and its aqueous suspension is neutralised with conc. aqueous ammonia under cooling. The precipitate is filtered off and the free amine is extracted with ether. Yield, 0.7 g (32%) of the title ethylene derivative, m.p. 155–160°C.

1-(5-Nitro-2-furyl)-1-phenylsulfonyl-2-[5-(4-isothiocyanatophenyl)-2-furyl]ethylene

Into a mixture of chloroform (50 ml) and thiophosgene (0.61 g; 0.005 mol) there is added with stirring a suspension of the amine hydrochloride (2.3 g; 0.005 mol; see the preceding paragraph) in water, the pH value being maintained at 6–6.5 by additions of sodium hydrogen carbonate. The chloroform layer is separated, washed with 10% aqueous hydrochloric acid and then water till neutral, dried over anhydrous sodium sulfate, and purified by chromatography on a column (20 cm; 2 cm in diameter) of alumina (Brockmann activity II). Yield, 1.1 g (46%) of the title isothiocyanate, m.p. 170–174°C (chloroform).

Spectral Measurements

The IR spectra were taken on a UR-20 Zeiss Jena spectrophotometer (polystyrene foil calibration; concentration of test substances in chloroform,  $10^{-2}$  M; 1.02 mm sodium chloride cell; accuracy,  $\pm 2$  cm $^{-1}$ ). The electron absorption spectra were measured on a recording Specord UV VIS Zeiss spectrophotometer in ethanol (concentration of test substances,  $2.5$ – $4.0 \cdot 10^{-5}$  M; 1 cm cells; accuracy,  $\pm 1$  nm).

REFERENCES

1. Jurášek A., Kováč J., Krutošiková A., Hrdina M.: This Journal 37, 3144 (1972).
2. Jurášek A., Kováč J.: This Journal 38, 1705 (1973).
3. Raffauf R. D.: J. Am. Chem. Soc. 72, 723 (1950).
4. Brand J. C. D., Eglinton G.: *Applications of Spectroscopy to Organic Chemistry*. Russian translation, p. 212. Mir, Moscow 1967.
5. Krutošiková A., Kováč J., Frimm R., Kováč Š., Sticzay T.: Chem. zvesti 25, 142 (1971).
6. Amiel Y.: J. Org. Chem. 36, 3691, 3697 (1971).
7. Cross A. H. J., Stevens S. G. R., Watts T. H. E.: J. Appl. Chem. 7, 562 (1957).

Translated by J. Pliml.