

A. Stanishauskaite, V. Getautis, A. Railaite^a

INVESTIGATION OF 3-(CARBAZOL-9-YL)-1,2-EPITHIOPROPANE INTERACTION WITH AROMATIC AMINES

In the reaction of 9-(2,3-epithiopropyl)-9H-carbazole with aromatic amines (aniline, 4-methoxy-, 4-methyl-, 4-fluoro-, 4-bromo-, 4-chloro-, 3-chloro-, 2-chloroaniline) and subsequent oxidation of the mixtures formed of propanethiols and disulfides with 25% H₂O₂ in basic solutions the respective disulfides have been synthesized. Carbazolyl-containing derivatives of the thiazolidine have been obtained.

Keywords: carbazole, aromatic amines, propanethiols, disulfides, thiazolidines.

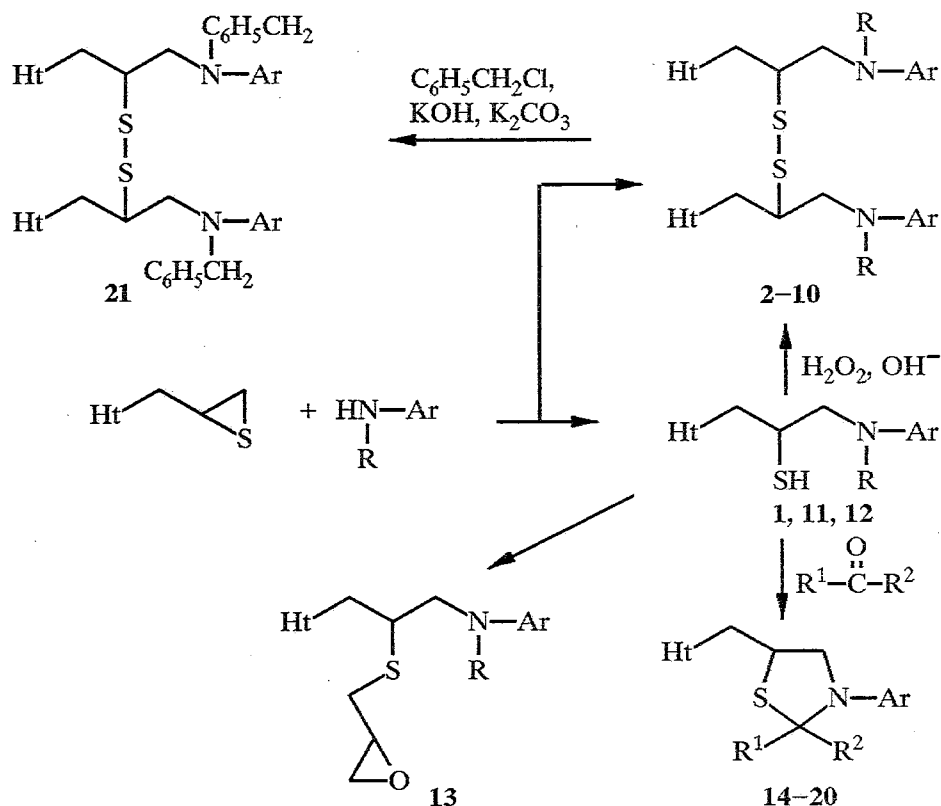
Epithio compounds are converted to aminothiols in the reaction with aromatic amines. These aminothiols are not stable and already under the influence of air oxygen undergo oxidation to form the respective disulfides. Hitherto, interaction of aliphatic and aromatic epithio compounds with aliphatic and aromatic amines has been mainly investigated [1–4].

We have performed the reaction of 9-(2,3-epithiopropyl)-9H-carbazole (ETPC) with amines and studied the properties of the products obtained.

After ETPC heating with excess of aniline (1:5) in boiling toluene for 3–4 h 3-anilino-1-(carbazol-9-yl)propane-2-thiol (**1**) was obtained as a main product with 5–60% yield. Besides, about 18% of bis(3,3¹-anilino-1,1¹-bis(carbazol-9-yl)diprop-2-yl disulfide (**2**) was isolated from the reaction mixture. Products **1**, **2** were formed in a similar ratio when carrying out the reaction at room temperature, but in this case the reaction time was 20–24 days.

Under the above conditions the reactions of 4-fluoro-, 4-bromo-, 3-chloro-, 2-chloro-, 4-methyl-, and 4-methoxyanilines with ETPC resulted in the mixtures of the respective propanethiols and disulfides, and an attempt was made to separate them by multiple crystallization or column chromatography on silicagel. However, the attempts to isolate pure propanethiols failed due to a partial oxidation to respective disulfides by air oxygen. To obtain disulfides the reaction mixtures were treated with hydrogen peroxide in the presence of sodium hydroxide. Thus, 1,1¹-bis(carbazol-9-yl)-3,3¹-bis(4-fluoroanilino)-diprop-2-yl disulfide (**3**), 3,3¹-bis(4-bromoanilino)-1,1¹-bis(carbazol-9-yl)diprop-2-yl disulfide (**4**), 1,1¹-bis(carbazol-9-methyl)-3,3¹-bis(4-chloroanilino)-diprop-2-yl disulfide (**5**), 1,1¹-bis(carbazol-9-yl)-3,3¹-bis(3-chloroanilino)-diprop-2-yl disulfide (**6**), 1,1¹-bis(carbazol-9-yl)-3,3¹-bis(2-chloroanilino)-diprop-2-yl disulfide (**7**), 1,1¹-bis(carbazol-9-yl)-3,3¹-bis(4-methylanilino)-diprop-2-yl disulfide (**8**), and 1,1¹-bis(carbazol-9-yl)-3,3¹-bis(4-methoxyanilino)-diprop-2-yl disulfide (**9**) were obtained. In the case of 1-naphthylamine derivative oxidation of propanethiol formed was much easier and only 1,1¹-bis(carbazol-9-yl)-3,3¹-bis(1-naphthylamino)-diprop-2-yl disulfide (**10**) was isolated from the reaction mixture.

It was found that duration of the reaction depends on amine nucleophilic properties and increases in the following order: 4-methoxyaniline, aniline, 4-methyl-, 4-fluoro-, 4-bromo-, 4-chloro-, 3-chloro-, 2-chloroaniline. The order presented reveals that 4-methoxyaniline reacts with ETPC most easily but 2-chloroaniline with much difficulty. Diphenylamine and *p*-nitroaniline do not react with ETPC under the conditions described above. 2-, 3-, 4-Aminopyridines characterized by strong nucleophilic properties initiate ETPC polymerization already at room temperature, and after 0,5 h only polymeric compounds can be isolated from the reaction mixture.



Ar = 1, 2, 14–18, 21 C₆H₅; 3, 19 4-FC₆H₄; 4 4-BrC₆H₄;
 5 4-ClC₆H₄; 6, 20 3-ClC₆H₄; 7 2-ClC₆H₄; 8 4-CH₃C₆H₄;
 9 4-CH₃OC₆H₄; 10 1-C₁₀H₇; R = 1–10 H; 11, 13 CH₃;
 12 C₂H₅; 14, 19, 20 R¹ = R² = H; 15–18 R¹ = H;
 R² = 15, 16 C₆H₅; 17 *p*-(C₂H₅)₂NC₆H₄; 18 2-furyl;
 1–21 Ht = carbazol-9-yl

Besides primary amines ETPC reacted with secondary amines, for example, with *N*-methyl- and *N*-ethylanilines. In this case the formed propanethiols oxidized more hard, and derivatives of 1-(carbazol-9-yl)-3-(*N*-methylanilino)-2-propanethiol (11) and 1-(carbazol-9-yl)-3-(*N*-ethylanilino)-2-propanethiol (12) were isolated from the reaction mixtures.

Characterization of compounds 1—21

Compound	Melting point, °C (solvent)	Molecular formula	Found. % Calculated, %					Yield, %	
			C	H	Hal	N	S	g	%
1	107.5—108.5 (toluene—2-propanol, 1 : 2)	C ₂₁ H ₂₀ NS	<u>76.19</u>	<u>6.01</u>	—	<u>7.99</u>	<u>9.81</u>	19 (A)	57.2 (A)
			75.87	6.06	—	8.43	9.64	20 (B)	60.3 (B)
2	148.5—150.0 (toluene—2-propanol, 2 : 1)	C ₄₂ H ₃₈ N ₄ S ₂	<u>76.92</u>	<u>5.56</u>	—	<u>8.83</u>	<u>9.71</u>	6 (A)	18.2 (A)
			76.10	5.78	—	8.45	9.67	3.3 (C)	100 (C)
3	193.5—165.5 (toluene—trichloromethane, 1 : 2)	C ₄₂ H ₃₆ F ₂ N ₄ S ₂	<u>72.56</u>	<u>5.04</u>	—	<u>7.93</u>	—	2.8	81.5
			72.18	5.19	—	8.02	—	—	—
4	152.5—153.5 (toluene)	C ₄₄ H ₄₂ N ₄ O ₂ S ₂	<u>73.28</u>	<u>5.74</u>	—	<u>7.93</u>	—	3.1	86.0
			73.10	5.86	—	7.75	—	—	—
5	182.0—183.5 (toluene—2-propanol, 2 : 1)	C ₄₄ H ₄₂ N ₄ S ₂	<u>76.31</u>	<u>6.32</u>	—	<u>8.02</u>	—	2.8	81.0
			76.49	6.12	—	8.11	—	—	—
6	198.5—199.5 (toluene—acetone, 2 : 1)	C ₄₂ H ₃₆ Br ₂ N ₄ S ₂	<u>61.61</u>	<u>4.47</u>	<u>19.51</u>	<u>6.94</u>	—	2.9	71.5
			61.47	4.42	19.47	6.83	—	—	—
7	196.5—198.5 (toluene)	C ₄₂ H ₃₆ Cl ₂ N ₄ S ₂	<u>69.22</u>	<u>5.05</u>	<u>10.10</u>	<u>7.87</u>	—	2.4	65.1
			68.93	4.96	9.69	7.66	—	—	—
8	154.0—156.0 (toluene—2-propanol, 2 : 1)	C ₄₂ N ₃₆ Cl ₂ N ₄ S ₂	<u>69.11</u>	<u>4.99</u>	<u>10.13</u>	<u>7.59</u>	—	2.1	58.2
			68.93	4.96	9.69	7.66	—	—	—
9	180.5—182.0 (toluene)	C ₄₂ N ₃₆ Cl ₂ N ₄ S ₂	<u>69.21</u>	<u>4.82</u>	<u>10.14</u>	<u>7.83</u>	—	2.3	63.1
			68.93	4.96	9.69	7.66	—	—	—
10	180.5—182.5 (toluene—2-propanol, 2 : 1)	C ₅₀ H ₄₂ N ₄ S ₂	<u>78.01</u>	5.93	—	<u>7.10</u>	—	3.3	43.5
			78.71	5.55	—	7.34	—	—	—

11	97.0—98.5 (toluene—2-propanol, 2 : 1)	$C_{22}H_{22}N_2S$	<u>76.52</u> 76.26	<u>6.13</u> 6.40	—	<u>7.91</u> 8.09	— 9.25	8.7	63.0
12	91.0—92.5 (toluene—ethanol, 1.5 : 2)	$C_{23}H_{24}N_2S$	<u>76.82</u> 76.63	<u>6.83</u> 6.71	—	<u>7.83</u> 7.77	— 8.89	8.0	55.6
13	Oil	$C_{25}H_{26}N_2OS$	<u>74.81</u> 74.59	<u>6.35</u> 6.51	—	<u>7.07</u> 6.96	— 7.96		
14	156.5—158 (toluene—2-propanol, 2 : 3)	$C_{22}H_{20}N_2S$	<u>76.77</u> 76.71	<u>5.80</u> 5.85	—	<u>8.07</u> 8.13	<u>9.36</u> 9.31	3.2	
15	156.0—157.0 (toluene—acetone, 1 : 1)	$C_{24}H_{24}N_2S$	<u>77.59</u> 77.38	<u>6.68</u> 6.49	—	<u>7.31</u> 7.52	<u>8.42</u> 8.61	3.3	89.0
16	142.5—144.0 (toluene—2-propanol, 1 : 1)	$C_{28}H_{24}N_2S$	<u>80.07</u> 79.96	<u>5.71</u> 5.75	—	<u>6.79</u> 6.66	<u>7.43</u> 7.63	3.0	71.0
17	136.5—137.5 (toluene—2-propanol, 2 : 1)	$C_{32}H_{33}N_3S$	<u>78.25</u> 78.17	<u>6.82</u> 6.76	—	<u>8.33</u> 8.55	<u>6.69</u> 6.52	3.8	77.2
18	138.0—140.0 (toluene—2-propanol, 2: 1)	$C_{26}H_{22}N_2OS$	<u>76.41</u> 76.07	<u>5.47</u> 5.40	—	<u>7.01</u> 6.82	— 7.81	3.6	87.8
19	175.0—176.5 (toluene—2-propanol, 1 : 1)	$C_{22}H_{19}FN_2S$	<u>72.69</u> 71.90	<u>5.19</u> 5.24	<u>5.55</u> 5.24	<u>7.93</u> 7.73	— 8.85	2.1	58.3
20	121.5—123.0 (toluene—2-propanol, 2 : 1)	$C_{22}H_{19}ClN_2S$	<u>70.05</u> 69.74	5.10 5.05	<u>9.66</u> 9.36	<u>7.50</u> 7.39	— 8.46	3.1	82.2
21	61—63	$C_{36}H_{50}N_4S_2$	79.82 79.77	6.05 5.98	—	<u>6.82</u> 6.64	— 7.60	7.3	86.5

Data of ^1H , ^{13}C , UV and IR spectra

Compound	^1H NMR spectra (CDCl_3), δ , ppm	UV spectra, λ_{max} , nm ($\lg \epsilon$)	IR spectra, ν , cm^{-1}
1	2	3	3
1			3390 (NH); 3065, 3047, 3010 (=C-H); 2960, 2935 (SH); 1595 (C=C, C-N); 760, 730, 694 (C=C of carbazole and monosubstituted benzene)
2	2.85–3.69 m (6H, CHCH_2NH); 4.13–4.54 m (4H, Ht- CH_2); 6.00–7.50 m (24H $\text{CH}_{\text{Ht,Ar}}$, NH); 7.80–8.13 m (4H, 4-H, 5-H Ht)	237.0 (4.95); 260.0 (4.61); 293.3 (4.53); 327.8 (3.91); 341.9 (3.94)	3430 (NH); 3060, 3030, 3010 (=C-H); 2940, 2920, 2880 (CH_{alif}); 1635, 1610 (C=C of carbazole and monosubstituted benzene)
3	2.83–3.78 m (6H, CHCH_2NH); 4.10–4.61 m (4H, Ht- CH_2); 5.90–7.50 m (22H $\text{CH}_{\text{Ht,Ar}}$, NH); 8.03 d (4H, 4-H, 5-H Ht, $J = 8$ Hz)	237.8 (4.93); 260.7 (4.56); 293.3 (4.52); 327.8 (3.91); 341.9 (3.92)	3400 (NH); 3065, 3050, 3010 (=C-H); 2910, 2890, 2850 (CH_{alif}); 1625, 1593 (CH=CH, C-N); 818 (C=C of <i>p</i> -disubstituted benzene); 755, 725 (CH=CH of carbazole)
4	2.95–3.23 m (4H, CH_2NH); 3.23–3.73 m (2H, CH-S-S-CH); 3.58 s (6H, OCH_3); 4.41 d (4H, Ht- CH_2 , $J = 7$ Hz); 6.33 dd (8H, AA^1BB^1 system, $J_{\text{AB}} = 8$ Hz); 7.00–7.48 m (14H, CH_{Ht} , NH); 7.88–8.13 m (4H, 4-H, 5-H Ht)	237.7 (5.00); 260.0 (4.63); 293.8 (4.52); 327.9 (4.00); 342.3 (3.96)	3400 (NH); 3050, 3040, 3010 (=C-H); 2940, 2915, 2890 (CH_{alif}); 1620, 1593 (CH=CH, C-N); 818 (C=C of <i>p</i> -disubstituted benzene); 750, 725 (CH=CH of carbazole)
5	2.08 s (6H, CH_3); 2.83–3.15 m (4H, CH_2NH); 3.15–3.73 m (2H, CH-S-S-CH); 4.26 d (4H, Ht- CH_2 , $J = 7$ Hz); 6.44 dd (8H, AA^1BB^1 system, $J_{\text{AB}} = 8$ Hz); 6.98–7.46 m (14H, CH_{Ht} , NH); 7.88–8.09 m (4H, 4-H, 5-H Ht)	237.2 (4.94); 260.0 (4.59); 293.3 (4.50); 328.0 (3.91); 341.9 (3.94)	3380 (NH); 3035, 3005 (=C-H); 2920, 2900, 2850 (CH_{alif}); 1615, 1590 (CH=CH, C-N); 805 (C=C of <i>p</i> -disubstituted benzene); 750, 720 (CH=CH of carbazole)
6	2.79–3.79 m (6H, CHCH_2NH); 4.21–4.79 m (4H, Ht- CH_2); 5.90–7.71 m (22H $\text{CH}_{\text{Ht,Ar}}$, NH); 7.94–8.29 m (4H, 4-H, 5-H Ht)	237.9 (5.04); 260.2 (4.84); 293.8 (4.59); 316.0 (3.92); 327.9 (3.98); 342.3 (4.01)	3410 (NH); 3040, 3020, 3010 (=C-H); 2940, 2920, 2860 (CH_{alif}); 1620, 1595 (CH=CH, C-N); 812 (C=C of <i>p</i> -disubstituted benzene); 755, 725 (CH=CH of carbazole)
7	2.80–3.71 m (6H, CHCH_2NH); 4.18–4.60 m (4H, Ht- CH_2); 6.59 dd (8H, AA^1BB^1 system, $J_{\text{AB}} = 8.00$ Hz); 6.78–7.65 m (14H $\text{CH}_{\text{Ht,Ar}}$, NH); 8.11 d (4H, 4-H, 5-H Ht, $J = 7$ Hz)	237.7 (5.00); 258.7 (4.80); 293.8 (4.55); 316.0 (3.89); 327.9 (3.95); 342.3 (3.96)	3400 (NH); 3055, 3045, 3010 (=C-H); 2930, 2910, 2860 (CH_{alif}); 1622, 1595 (CH=CH, C-N); 822 (C=C of <i>p</i> -disubstituted benzene); 755, 725 (CH=CH of carbazole)

8	2.99–3.88 m (6H, CHCH_2NH); 4.24–4.88 m (4H, Ht- CH_2); 5.79–7.59 m (22H $\text{CH}_{\text{Ht,Ar}}$, NH); 7.84–8.29 m (4H, 4-H, 5-H Ht, $J = 7$ Hz)	234.6 (4.69); 260.0 (4.57); 293.3 (4.53); 328.2 (3.89); 342.1 (3.96)	3390 (NH); 3050, 3010 (=C–H); 2920, 2860 (CH_{alif}); 1600, 1595 ($\text{CH}=\text{CH}$, C–N); 835 (C=C of <i>o</i> -disubstituted benzene); 750, 725 ($\text{CH}=\text{CH}$ of carbazole)
9	2.99–3.88 m (6H, CHCH_2NH); 4.10–4.53 m (4H, Ht- CH_2); 5.90–7.60 m (22H $\text{CH}_{\text{Ht,Ar}}$, NH); 7.88–8.34 m (4H, 4-H, 5-H Ht).	237.7 (5.00); 258.7 (4.69); 293.8 (4.56); 328.4 (3.92); 342.3 (3.95)	3410 (NH); 3065, 3045, 3020 (=C–H); 2950, 2925, 2900 (CH_{alif}); 1625, 1600 ($\text{CH}=\text{CH}$, C–N); 775 (C=C of <i>m</i> -disubstituted benzene); 755, 728 ($\text{CH}=\text{CH}$ of carbazole)
10	2.93–3.39 m (CH_2NH); 3.39–4.14 m (2H, CH-S-S-CH); 4.14–4.63 m (4H, Ht- CH_2); 5.85–7.86 m (28H $\text{CH}_{\text{Ht,Ar}}$, NH); 7.86–8.23 m (4H, 4-H, 5-H Ht)	230.0 (5.07); 237.5 (5.07); 294.2 (4.59); 329.7 (4.37); 341.4 (4.33)	3410 (NH); 3070, 3045, 3018 (=C–H); 2930, 2920, 2880 (CH_{alif}); 1595, 1582 ($\text{CH}=\text{CH}$, C–N); 788, 775 ($\text{CH}=\text{CH}$ of naftalene); 750, 725 ($\text{CH}=\text{CH}$ of carbazole); 568 (C–S)
11	1.4 d (H, SH); 2.84 s (3H, CH_3); 3.15–3.49 m (2H, CH_2N); 3.49–4.00 m (1H, CH_2CHCH_2); 4.13–4.38 m (2H, Ht- CH_2); 6.28–7.50 m (11H, $\text{CH}_{\text{Ht,Ar}}$); 7.85–8.10 m (2H, 4-H, 5-H Ht)	237.7 (4.71); 260.5 (4.49); 293.8 (4.28); 313.0 (3.55); 328.8 (3.63); 342.3 (3.65)	3040–3100, 3010 (=C–H); 2930, 2910 (CH_{aliph}); 2550 (SH); 1595, 1566 (C=C, C–N); 750, 725, 698 ($\text{CH}=\text{CH}$ of carbazole and monosubstituted
12		240.0 (4.79); 261.8 (4.69); 295.0 (4.52); 331.8 (3.91); 345.0 (3.95)	3070, 3040, 3022 (=C–H); 2940, 2905, 2870 (CH_{alif}); 2552 (SH); 1618, 1590, (C=C, C–N); 750, 722, 690 ($\text{CH}=\text{CH}$ of carbazole and monosubstituted benzene)
13	1.70–3.08 m, 2.98 s (6H, $\text{CHCH}_2\text{NCH}_3$); 3.08–3.90 m (5H, $\text{SCH}_2\text{CHCH}_2$); 4.08–4.60 m (2H, Ht- CH_2); 5.15–7.63 m (11H $\text{CH}_{\text{Ht,Ar}}$); 7.91 (2H, 4-H, 5-H Ht, $J = 7$ Hz)	238.4 (4.74); 260.0 (4.45); 293.8 (4.26); 329.0 (3.65); 344.9 (3.69)	3050, 3018 (=C–H); 2920, 2890, 2850 (CH_{alif}); 1625, 1595, (C=C, C–N); 755, 725, 698 ($\text{CH}=\text{CH}$ of carbazole and monosubstituted benzene)
14	3.33 (2H, ABX system, CH_2NPh , $J_{\text{AB}} = 11$ Hz, $J_{\text{AX}} = 3$ Hz, $J_{\text{BX}} = 5$ Hz, H_{trans} and H_{cis}); 3.73–4.08 m (1H, CH_2CHCH_2); 4.08–4.78 m (4H, Ht- CH_2 , SCH_2N); 6.48–7.63 m (11H $\text{CH}_{\text{Ht,Ar}}$); 7.80–8.11 (2H, 4-H, 5-H Ht)	237.9 (4.69); 261.6 (4.41); 294.2 (4.25); 330.1 (3.63); 343.7 (3.68)	3063, 3040, 3030 (=C–H); 2970, 2928, 2852 (CH_{alif}); 1596, (C=C, C–N); 748, 726, 690 ($\text{CH}=\text{CH}$ of carbazole and monosubstituted benzene)
15	1.19 s; 1.69 s (6H, CH_3); 3.25 (2H, ABX system, CH_2NPh , $J_{\text{AB}} = 10$ Hz, $J_{\text{AX}} = 5$ Hz, $J_{\text{BX}} = 3$ Hz, H_{trans} and H_{cis}); 3.49–3.74 m (1H, CH_2CHCH_2); 4.35 (2H, $\text{A}^1\text{B}^1\text{X}$ system, Ht- CH_2 , $J_{\text{A}^1\text{B}^1} = 15$ Hz, $J_{\text{A}^1\text{X}} = 10$ Hz, $J_{\text{B}^1\text{X}} = 4.5$ Hz); 6.22–7.33 m (11H $\text{CH}_{\text{Ht,Ar}}$); 7.76–8.00 (2H, 4-H, 5-H Ht)	238.1 (4.76); 258.7 (4.47); 293.8 (4.31); 328.8 (3.66); 342.8 (3.71)	3055, 3035, 3020 (=C–H); 2970, 2930, 2855 (CH_{alif}); 1620, 1590, (C=C, C–N); 755, 730, 710 ($\text{CH}=\text{CH}$ of carbazole and monosubstituted benzene)

1	2	3	4
16	3.65-4.00 m (2H, $\text{CHCH}_2\text{N-Ar}$); 4.00-4.65 m (3H, Ht- CH_2CH); 6.13 s (1H, ArCH); 6.35-7.90 m (16H, $\text{CH}_{\text{Ht,Ar}}$); 7.90-8.14 m (2H, 4-H, 5-H Ht)	238.4 (4.74); 261.3 (4.43); 285.0 (4.30); 293.8 (4.31); 329.0 (3.71); 344.9 (3.67); 416.7 (3.77)	3060, 3050, 3030 (=C-H); 2970, 2920, 2860 (CH_{alif}); 1630, 1605, (C=C, C-N); 760, 735, 705 (CH=CH of carbazole and monosubstituted benzene)
17	0.98; 1.06 two triplets (6H, CH_3CH_2 , $J = 7$ Hz); 3.19, 3.29 two quartets (4H, CH_2CH_2 , $J = 7$ Hz); 3.50-4.18 m (3H, CHCH_2N); 4.36-4.60 m (2H, Ht- CH_2); 5.81, 6.08 two s (1H, ArCH(S)NH); 6.38-7.66 m (15H $\text{CH}_{\text{Ht,Ar}}$); 7.90-8.13 m (2H, 4-H, 5-H Ht)	238.4 (4.71); 260.0 (4.42); 293.8 (4.28); 329.0 (3.64); 344.1 (3.69)	3060, 3048, 3020 (=C-H); 2960, 2924, 2864 (CH_{alif}); 1608, 1593 (C=C, C-N); 824 (CH=CH of <i>p</i> -substituted benzene); 744, 724, 692 (CH=CH of carbazole and monosubstituted benzene)
18	3.48-3.90 m (2H, $\text{CHCH}_2\text{N-Ar}$); 3.90-4.65 m (4H, Ht- CH_2CH , SCHN); 6.04-6.29 m (3H, CH of furan); 6.58-7.56 m (11 H, $\text{CH}_{\text{Ht,Ar}}$); 7.95-8.20 m (2H, 4-H, 5-H Ht)		3035, 3005 (=C-H); 2918, 2850 (CH_{alif}); 1595 (C=C, C-N); 745, 726, 690 (CH=CH of carbazole and monosubstituted benzene)
19	3.35 (2H, ABX system, CH_2NPh , $J_{\text{AB}} = 10$ Hz, $J_{\text{AX}} = 10$ Hz, $J_{\text{BX}} = 6$ Hz, H_{trans} and H_{cis}); 3.84-4.14 m (1H, CH_2CHCH_2); 4.14-4.88 m (2H, Ht- CH_2); 4.41 s (2H, SCH_2N); 6.46-7.75 m (10H, $\text{CH}_{\text{Ht,Ar}}$); 7.94-8.19 m (2H, 4-H, 5-H Ht)	221,6 (4,52); 238.4 (4,66); 248.3 (4,53); 261.7 (4,51); 293.8 (4,30); 329.0 (3,64); 344.1 (3,69)	3035, 3010 (=C-H); 2925, 2900 2835 (CH_{alif}); 1592 (C=C, C-N); 818 (CH=CH of <i>p</i> -disubstituted benzene); 755, 725, (CH=CH of carbazole)
20	3.35 (2H, ABX system, CH_2NPh , $J_{\text{AB}} = 10$ Hz, $J_{\text{AX}} = 2$ Hz, $J_{\text{BX}} = 5$ Hz, H_{trans} and H_{cis}); 3.75-4.11 m (1H, CH_2CHCH_2); 4.11-4.81 m (2H, Ht- CH_2); 4.34 s (2H, SCH_2N); 6.29-7.75 m (10H, $\text{CH}_{\text{Ht,Ar}}$); 7.91-8.16 m (2H, 4-H, 5-H Ht)		3035, 3010 (=C-H); 2920, 2850 (CH_{alif}); 1590, 1560 (C=C, C-N); 775 (CH=CH of <i>m</i> -disubstituted benzene); 750, 725, (CH=CH of carbazole)
21	3.06-3.94 m (6H, CHCH_2NAr); 3.94-4.69 m (8H, Ht- CH_2 , Ar CH_2N); 6.06-7.69 m (32H, $\text{CH}_{\text{Ht,Ar}}$); 7.69-8.19 m (4H, 4-H, 5-H Ht)		3042, 3031, 3010 (=C-H); 2911, 2850 (CH_{alif}); 1623, 1595 (C=C, C-N); 750, 725, 695 (CH=CH of carbazole and monosubstituted benzene)

The reaction with N-ethylaniline proceeds considerably longer than with aniline (28 and 130 h), apparently, because of steric hindrances.

The structure of propanethiols **1**, **11**, and **12** disulfides **2—10** were confirmed by elemental analysis, the data of ^1H and ^{13}C NMR, IR, UV spectra. In the IR spectra of propanethiols **1**, **11**, and **12** SH group exhibited characteristic peaks at 2553, 2550, and 2552 cm^{-1} , respectively, and in that of propanethiol **1** NH group also gave a peak at 3390 cm^{-1} . In disulfides **2—10** absorption peaks in the area of 3380—3430 cm^{-1} are characteristic for an NH group, in their ^1H NMR spectra signals specific for protons of HtCH_2 , ArNHCH_2 and CH—S—S—CH were observed in the area of 2,65—4,88 ppm. In disulfides **4** and **5** OCH_3 and CH_3 groups displayed singlets at 3,58 and 2,08 ppm, respectively, in the latter and in disulfide **7** AA^1BB^1 systems characteristic of protons of *p*-disubstituted benzenes which centers at 6,33 ($J_{\text{AB}} = 9$ Hz), 6,44 ($J_{\text{AB}} = 8$ Hz), 6,59 ($J_{\text{AB}} = 8$ Hz) ppm were observed. In UV spectra all the absorption maxima characteristics of carbazolyl chromophore were observed. Lines in ^{13}C NMR spectra fairly exactly matched those calculated theoretically.

Besides the spectral analysis the structure of propanethiols **1**, **11** was confirmed by some chemical transformations. By the action of 1-chloro-2,3-epoxypropane (CEP) on propanethiol **11** the hydrogen of SH group was replaced by epoxypropyl group, and 5-(carbazolyl-9-methyl)-1,2-epoxy-6-(N-methylanilino)-4-thiahexane (**13**) was obtained.

By the action of formaldehyde, acetone, benzaldehyde, 4-diethylaminobenzaldehyde and 2-furaldehyde on propanethiol **1** at room temperature carbazolyl-containing thiazolidine derivatives **14—18** were synthesized.

The corresponding thiazolidine derivatives (**19**, **20**) were isolated after treating with a formalin excess the mixtures obtained by the action of 4-fluoroaniline and also 3-chloroaniline on ETPC. It was noticed that the reaction of propanethiol **1** with acetone was initiated by the sun light and did not take place in darkness.

By disulfide **2** alkylation with benzyl chloride dibenzylated derivative, 3,3 1 -bis(benzylphenylamino)-1,1 1 -bis(carbazol-9-yl)diprop-2-yl disulfide (**21**) was obtained. Compound **21** was tested as an organic photoconductor for production of electrophotographic layers and exhibited a comparatively not bad photosensitivity ($S_{345} = 30$, $S_{125} = 24$ m^2/J) and good physicomechanical properties.

EXPERIMENTAL

^1H NMR spectra were recorded on a Hitachi R-22 spectrometer (90 MHz), Tesla BS 487C (80 MHz), and presented in Table 2 (multiplicity, number of atoms, group, coupling constant in Hz), ^{13}C NMR spectra on a Tesla BS 567A (25.142 MHz), IR spectra on UR-20, Specord M80 spectrometer for KBr pellets. The course of reaction and the purity of products were controlled by thin-layer chromatography on Silufol UV-254 (Kavalier) plates.

Synthesis of 3,3 1 -bis(R-phenylamino)-1,1 1 -bis(carbazol-9-yl)diprop-2-yl disulfide (2—9). The mixture of 0.01 mole of ETPC, 0.05 mole of aromatic amine (ratio 1:5) and 25 ml of toluene was kept at room temperature (method A) or was heated at temperature 105—110°C (method B). Mixture was washed with 10% solution of HCl to remove the excess of aromatic amine, toluene

was distilled off, 1—1.5 ml 25% H₂O₂ and 20 ml 0.2N NaOH was added and the mixture was kept at room temperature. The precipitate of 2—9 was filtered off, washed with water (to neutral reaction), dried and recrystallized. In the case of aniline at room temperature after 24 h and at toluene boiling temperature after 3—4 h 3-anilino-1-(carbazol-9-yl)-2-propanethiol (1) (50—65%) and 3,3-bisanilino-1,1¹-bis(carbazol-9-yl)diprop-2-yl disulfide (2) (18%) were obtained.

3,3¹-Bis(1-naphthylamino)-1,1¹-bis(carbazol-9-yl)diprop-2-yl disulfide (10). ETPC (2.4 g, 0.01 mol) was dissolved in 25 ml of toluene, 1-naphthylamine (7.1 g, 0.05 mol) was added and the mixture was heated for 65 h at 105—110°C, then the mixture was washed with 10% hydrochloric acid, toluene was distilled off, the precipitate of 10 was filtered off and washed with ethanol.

1-(Carbazol-9-yl)-3-(N-methylphenylamino)-2-propanethiol (11), 3-(N-ethylphenylamino)-1-(carbazol-9-yl)-2-propanethiol (12). ETPC (9.6 g, 0.04 mol) was dissolved in 40 ml of toluene, N-methylphenylamine (17 g, 0.16 mol) or N-ethylphenylamine (19.4 g, 0.16 mol) was added to the solution and the mixture was heated for 28 (130) h at 100—105 °C (TLC control using diethyl ether—acetone—hexane, 2:2:1 system). The mixture was washed with 60 ml of 10% hydrochloric acid, toluene was distilled off, precipitates 11, 12 filtered off and washed with 2-propanol.

1,2-Epoxy-5-(carbazolyl-9-methyl)-6-(N-methylphenylamino)-4-thiahexane (13). The mixture of compound 11 (3.5 g, 0.01 mol), 15 ml of CEP and 3-4 drops of TEA was kept at room temperature. Then the CEP excess was distilled off and the product was purified by chromatography applying a column packed with silicagel Silpearl. A system of acetone-hexane 1:4, was used as an eluent.

3-Phenyl-5-(carbazolyl-9-methyl)thiazolidine (14). 9 ml (0.1 mol) of 40% formaline were added to a solution of compound 1 (3.3 g, 0.01 mol) in 30 ml of CHCl₃, and the mixture was stirred for 0.5 h at room temperature (TLC control with diethyl ether—hexane, 1:4 system). Then formaline was separated, trichloromethane distilled off, precipitate filtered off and washed with 2-propanol.

3-Phenyl-5-(carbazolyl-9-methyl)-2,2-dimethylthiazolidine (15). A solution of compound 1 (3.3 g, 0.01 mol) in 30 ml of acetone was kept at room temperature in the sun light (the control with acetone—hexane, 1:4 system). Precipitate of 15 was filtered off and washed with 2-propanol.

2,3-Diphenyl-5-(carbazolyl-9-methyl)thiazolidine (16). To a solution of compound 1 (3.3 g, 0.01 mol) in 30 ml of CHCl₃, benzaldehyde (5.3 g, 0.05 mol) of was added, and the mixture was kept for 2 h at room temperature (diethyl ether—hexane, 1:2). Then the mixture was treated with the NaHCO₃ solution, trichloromethane was distilled off, precipitate 16 was recrystallized.

2-(4-Diethylaminophenyl)-3-phenyl-5-(carbazolyl-9-methyl)thiazolidine (17). 4-(N,N-diethylamino)benzaldehyde (8.9 g, 0.05 mol), 2 g of K₂CO₃ were added to a solution of compound 1 (3.3 g, 0.01 mol) in 30 ml of toluene, and the mixture was stirred for 24 h at room temperature (diethyl ether—hexane, 1:2). Then mixture was washed with water, toluene was distilled off and residue was purified by chromatography using column packed with silica gel Silpearl. System of diethyl ether—hexane was used as an eluent. The product was recrystallized.

2-(2-Furyl)-3-phenyl-5-(carbazolyl-9-methyl)thiazolidine (18). 2-Furaldehyde (2 g, 0.02 mol) was added to a solution of compound 1 (3.3 g, 0.01 mol) in 30 ml of CHCl₃, and the mixture was stirred at room temperature (system diethyl ether—hexane, 1:1). Trichloromethane and 2-furaldehyde excess were distilled, precipitate filtered off and washed with a mixture of diethyl ether and hexane, 1:1.

3-(4-Fluorophenyl)-, 3-(3-chlorophenyl)-5-(carbazolyl-9-methyl)thiazolidines (19, 20). A solution of ETPC (2.4 g, 0.01 mol) and 4-fluoroaniline (4.7 ml, 0.05 mol) or 3-chloroaniline (6.4 g, 0.05 mol) in 25 ml toluene and mixture was heated at 100—105 °C (system diethyl ether—hexane, 1:2). Then the mixture was treated with 14 ml of 10% hydrochloric acid, toluene was distilled off, precipitate of thiazolidines 19, 20 was filtered off, dissolved in CHCl₃ and treated with formaline 40% solution excess. Compounds 19 and 20 were purified by the procedure described for 14.

3,3¹-Bis(benzylphenylamino)-1,1¹-bis(carbazol-9-yl)diprop-2-yl disulfide (21). The mixture of 18 (4.2 g, 0.005 mol), benzyl chloride (3.4 ml, 0.03 mol), K₂CO₃ (0.6 g, 0.005 mol) and 30 ml of 2-propanol was heated for 10 h at 80—85 °C (system diethyl ether—hexane, 1:2). Then the mixture extracted with toluene, toluene was distilled off, precipitate of 21 was filtered off and washed with ethanol.

REFERENCES

1. Г. И. Браз, *ЖОХ*, **21**, 688 (1951).
2. R. J. Winemann, M. H. Gollis, J. C. James, A. M. Pomponi, *J. Org. Chem.*, **27**, 4222 (1962).
3. J. M. Stewart, *J. Org. Chem.*, **28**, 596 (1963).
4. В. А. Муллин, А. И. Золотов, В. И. Шишкин, *Изв. вузов. Химия и хим. технология*, **23**, 41 (1980).

*Kaunas University of Technology,
Kaunas 3028, Lithuania
e-mail: alsta@vandenis-sc-uni.ktu.lt*

Received 28.10.98

^a *Joint-stock company "Achem",
Kaunas, Lithuania*
