*Chemistry of Heterocyclic Compounds, Vol. 36, No. 1, 2000*

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

**A. Stanishauskaite[1], V. Getautis[1], A. Railaite[2]**

*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%* $H_2O_2$ *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 the main product with 5-60% yield. Moreover, about 18% of bis(3,3'-anilino)-1,1'-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.

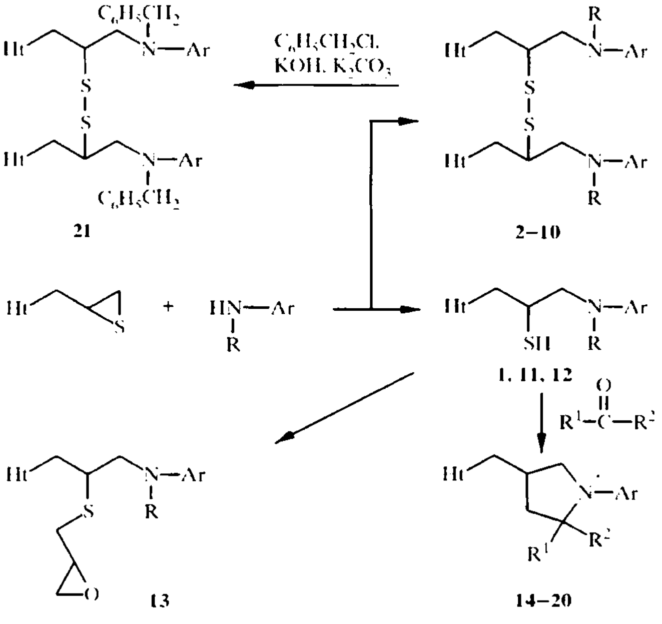
Under the above conditions the reactions of 4-fluoro-, 4-bromo-, 3-chloro-, 2-chloro-, 4-methyl-, and 4-methoxyanilines with ETPC resulted in mixtures of the respective propanethiols and disulfides, and an attempt was made to separate them by multiple crystallization or column chromatography on silicagel.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

It was found that the duration of the reaction depends on the nucleophilic properties of the amine and increases in the folloving 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

---

[1] Kaunas University of Technology, Kaunas 3028, Lithuania; e-mail: alsta@vandenis-sc-uni.ktu.lt. [2] Joint-stock company "Achem", Kaunas, Lithuania. Published in Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 90-99, January, 2000. Original article submitted October 28, 1998.

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** $C_6H_5$; **3**, **19** 4-$FC_6H_4$; **4** 4-$BrC_6H_4$; **5** 4-$ClC_6H_4$; **6**, **20** 3-$ClC_6H_4$; 7 2-$ClC_6H_4$; **8** 4-$CH_3C_6H_4$; **9** 4-$CH_3OC_6H_4$; **10** 1-$C_{10}H_7$; R = **1-10** H; **11**, **13** $CH_3$; **12** $C_2H_5$; **14**, **19**, **20** $R^1 = R^2$ = H; **15-18** $R^1$ = H; $R^2$ = **15**, **16** $C_6H_5$; **17** *p*-$(C_2H_5)_2NC_6H_4$; **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 propanethiols formed are oxidized with greater difficulty, 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.

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 and from the data of $^1$H and $^{13}$C NMR, IR, and UV spectra. In the IR spectra of propanethiols **1**, **11**, and **12** the SH group exhibited characteristic peaks at 2553, 2550, and 2552 cm$^{-1}$, respectively, and in that of propanethiol **1** the 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 $^1$H NMR spectra signals specific for protons of $HtCH_2$, ArNHCH, and CH–S–S–CH were observed in the area of 2.65-4.88 ppm. In disulfides **4** and **5** the $OCH_3$ and $CH_3$ groups displayed singlets at 3.58 and 2.08 ppm, respectively; in the latter and in disulfide 7 AA$^1$BB$^1$ systems characteristic of protons of *p*-disubstituted benzenes whith centers at 6.33 ($J_{AB}$ = 9 Hz), 6.44 ($J_{AB}$ = 8 Hz), and 6.59 ($J_{AB}$ = 8 Hz) ppm were observed. In the UV spectra all the absorption maxima characteristic of carbazolyl chromophore were observed. Lines in the $^{13}$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 the SH group was replaced by the epoxypropyl group, and 5-(carbazolyl-9-methyl)-1,2-epoxy-6-(N-methylanilino)-4-thiahexane (**13**) was obtained.

TABLE 1. Characteristics of Compounds **1-21**

| Compound | Empirical formula | Found, % / Calculated, % | | | | | mp, °C (solvent) | Yield, % | |
|---|---|---|---|---|---|---|---|---|---|
| | | C | H | Hal | N | S | | g | % |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| **1** | $C_{21}H_{20}NS$ | $\frac{76.19}{75.87}$ | $\frac{6.01}{6.06}$ | — | $\frac{7.99}{8.43}$ | $\frac{9.81}{9.64}$ | 107.5-108.5<br>(toluene–propan-2-ol, 1 : 2) | 19 (A)<br>20 (B) | 57.2 (A)<br>60.3 (B) |
| **2** | $C_{42}H_{38}N_4S_2$ | $\frac{76.92}{76.10}$ | $\frac{5.56}{5.78}$ | — | $\frac{8.83}{8.45}$ | $\frac{9.71}{9.67}$ | 148.5-150.0<br>(toluene–propan-2-ol, 2 : 1) | 6 (A)<br>3.3 (C) | 18.2 (A)<br>100 (C) |
| **3** | $C_{42}H_{36}F_2N_4S_2$ | $\frac{72.56}{72.18}$ | $\frac{5.04}{5.19}$ | — | $\frac{7.93}{8.02}$ | — | 193.5-165.5<br>(toluene–chloroform, 1 : 2) | 2.8 | 81.5 |
| **4** | $C_{44}H_{42}N_4O_2S_2$ | $\frac{73.28}{73.10}$ | $\frac{5.74}{5.86}$ | — | $\frac{7.93}{7.75}$ | — | 152.5-153.5<br>(toluene) | 3.1 | 86.0 |
| **5** | $C_{44}H_{42}N_4S_2$ | $\frac{76.31}{76.49}$ | $\frac{6.32}{6.12}$ | — | $\frac{8.02}{8.11}$ | — | 182.0-183.5<br>(toluene–propan-2-ol, 2 : 1) | 2.8 | 81.0 |
| **6** | $C_{42}H_{36}Br_2N_4S_2$ | $\frac{61.61}{61.47}$ | $\frac{4.47}{4.42}$ | $\frac{19.51}{19.47}$ | $\frac{6.94}{6.83}$ | — | 198.5-199.5<br>(toluene–acetone, 2 : 1) | 2.9 | 71.5 |
| **7** | $C_{42}H_{36}Cl_2N_4S_2$ | $\frac{69.22}{68.93}$ | $\frac{5.05}{4.96}$ | $\frac{10.10}{9.69}$ | $\frac{7.87}{7.66}$ | — | 196.5-198.5<br>(toluene) | 2.4 | 65.1 |
| **8** | $C_{42}N_{36}Cl_2N_4S_2$ | $\frac{69.11}{68.93}$ | $\frac{4.99}{4.96}$ | $\frac{10.13}{9.69}$ | $\frac{7.59}{7.66}$ | — | 154.0-156.0<br>(toluene–propan-2-ol, 2 : 1) | 2.1 | 58.2 |
| **9** | $C_{42}N_{36}Cl_2N_4S_2$ | $\frac{69.21}{68.93}$ | $\frac{4.82}{4.96}$ | $\frac{10.14}{9.69}$ | $\frac{7.83}{7.66}$ | | 180.5-182.0<br>(toluene) | 2.3 | 63.1 |
| **10** | $C_{50}H_{42}N_4S_2$ | $\frac{78.01}{78.71}$ | $\frac{5.93}{5.55}$ | — | $\frac{7.10}{7.34}$ | — | 180.5-182.5<br>(toluene–propan-2-ol, 2 : 1) | 3.3 | 43.5 |

TABLE 1 (continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| **11** | $C_{22}H_{22}N_2S$ | $\frac{76.52}{76.26}$ | $\frac{6.13}{6.40}$ | — | $\frac{7.91}{8.09}$ | $\frac{\text{—}}{9.25}$ | 97.0-98.5<br>(toluene–propan-2-ol, 2 : 1) | 8.7 | 63.0 |
| **12** | $C_{23}H_{24}N_2S$ | $\frac{76.82}{76.63}$ | $\frac{6.83}{6.71}$ | — | $\frac{7.83}{7.77}$ | $\frac{\text{—}}{8.89}$ | 91.0-92.5<br>(toluene–ethanol, 1.5 : 2) | 8.0 | 55.6 |
| **13** | $C_{25}H_{26}N_2OS$ | $\frac{74.81}{74.59}$ | $\frac{6.35}{6.51}$ | — | $\frac{7.07}{6.96}$ | $\frac{\text{—}}{7.96}$ | Oil | | |
| **14** | $C_{22}H_{20}N_2S$ | $\frac{76.77}{76.71}$ | $\frac{5.80}{5.85}$ | — | $\frac{8.07}{8.13}$ | $\frac{9.36}{9.31}$ | 156.5-158<br>(toluene–propan-2-ol, 2 : 3) | 3.2 | |
| **15** | $C_{24}H_{24}N_2S$ | $\frac{77.59}{77.38}$ | $\frac{6.68}{6.49}$ | — | $\frac{7.31}{7.52}$ | $\frac{8.42}{8.61}$ | 156.0-157.0<br>(toluene–acetone, 1 : 1) | 3.3 | 89.0 |
| **16** | $C_{28}H_{24}N_2S$ | $\frac{80.07}{79.96}$ | $\frac{5.71}{5.75}$ | — | $\frac{6.79}{6.66}$ | $\frac{7.43}{7.63}$ | 142.5-144.0<br>(toluene–propan-2-ol, 1 : 1) | 3.0 | 71.0 |
| **17** | $C_{32}H_{33}N_3S$ | $\frac{78.25}{78.17}$ | $\frac{6.82}{6.76}$ | — | $\frac{8.33}{8.55}$ | $\frac{6.69}{6.52}$ | 136.5-137.5<br>(toluene–propan-2-ol, 2 : 1) | 3.8 | 77.2 |
| **18** | $C_{26}H_{22}N_2OS$ | $\frac{76.41}{76.07}$ | $\frac{5.47}{5.40}$ | — | $\frac{7.01}{6.82}$ | $\frac{\text{—}}{7.81}$ | 138.0-140.0<br>(toluene–propan-2-ol, 2: 1) | 3.6 | 87.8 |
| **19** | $C_{22}H_{19}FN_2S$ | $\frac{72.69}{71.90}$ | $\frac{5.19}{5.24}$ | $\frac{5.55}{5.24}$ | $\frac{7.93}{7.73}$ | $\frac{\text{—}}{8.85}$ | 175.0-176.5<br>(toluene–propan-2-ol, 1 : 1) | 2.1 | 58.3 |
| **20** | $C_{22}H_{19}ClN_2S$ | $\frac{70.05}{69.74}$ | $\frac{5.10}{5.05}$ | $\frac{9.66}{9.36}$ | $\frac{7.50}{7.39}$ | $\frac{\text{—}}{8.46}$ | 121.5-123.0<br>(toluene–propan-2-ol, 2 : 1) | 3.1 | 82.2 |
| **21** | $C_{56}H_{50}N_4S_2$ | $\frac{79.82}{79.77}$ | $\frac{6.05}{5.98}$ | — | $\frac{6.82}{6.64}$ | $\frac{\text{—}}{7.60}$ | 61-63 | 7.3 | 86.5 |

TABLE 2. $^1$H, $^{13}$C, UV and IR Spectral Characteristics of Compounds **1-21**

| Compound | $^1$H NMR spectra (CDCl$_3$), δ, ppm | UV spectra, $\lambda_{max}$, nm (log ε) | IR spectra, ν, cm$^{-1}$ |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| **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, $C\underline{H}C\underline{H}_2NH$); 4.13–4.54 m (4H, Ht-CH$_2$); 6.00–7.50 m (24H CH$_{Ht,Ar}$, 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, $C\underline{H}C\underline{H}_2NH$); 4.10–4.61 m (4H, Ht-CH$_2$); 5.90-7.50 m (22H CH$_{Ht,Ar}$, 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 *p*-disubstituted benzene); 755, 725 (CH=CH of carbazole) |
| **4** | 2.95-3.23 m (4H, $C\underline{H}_2NH$); 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$^1$BB$^1$ system, $J_{AB}$ = 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 *p*-disubstituted benzene); 750, 725 (CH=CH of carbazole) |
| **5** | 2.08 s (6H, CH$_3$); 2.83-3.15 m (4H, $C\underline{H}_2NH$); 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$^1$BB$^1$ system, $J_{AB}$ = 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 *p*-disubstituted benzene); 750, 720 (CH=CH of carbazole) |
| **6** | 2.79-3.79 m (6H, $C\underline{H}C\underline{H}_2NH$); 4.21–4.79 m (4H, Ht-CH$_2$); 5.90–7.71 m (22H CH$_{Ht,Ar}$, 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 *p*-disubstituted benzene); 755, 725 (CH=CH of carbazole) |
| **7** | 2.80–3.71 m (6H, $C\underline{H}C\underline{H}_2NH$); 4.18–4.60 m (4H, Ht-CH$_2$); 6.59 dd (8H, AA$^1$BB$^1$ system, $J_{AB}$ = 8.00 Hz); 6.78–7.65 m (14H CH$_{Ht,Ar}$, 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 *p*-disubstituted benzene); 755, 725 (CH=CH of carbazole) |

TABLE 2 (continued)

| 1 | 2 | 3 | 4 |
|---|---|---|---|
| **8** | 2.99-3.88 m (6H, C$\underline{H}$C$\underline{H}_2$NH ); 4.24-4.88 m (4H, Ht-$CH_2$);<br>5.79-7.59 m (22H $CH_{Ht,Ar}$, 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 ($CH_{alk}$); 1600, 1595 (CH=CH, C–N);<br>835 (C=C of *o*-disubstituted benzene); 750, 725 (CH=CH of carbazole) |
| **9** | 2.99-3.88 m (6H, C$\underline{H}$C$\underline{H}_2$NH ); 4.10-4.53 m (4H, Ht-$CH_2$);<br>5.90-7.60 m (22H $CH_{Ht,Ar}$, 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 ($CH_{alk}$); 1625, 1600 (CH=CH, C–N); 775 (C=C of *m*-disubstituted benzene); 755, 728 (CH=CH of carbazole) |
| **10** | 2.93-3.39 m (C$\underline{H}_2$NH ); 3.39-4.14 m (2H, CH-S-S-CH);<br>4.14-4.63 m (4H, Ht-$CH_2$); 5.85-7.86 m (28H $CH_{Ht,Ar}$, NH);<br>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 ($CH_{alk}$); 1595, 1582 (CH=CH, C–N); 788, 775 (CH=CH of naphtalene); 750, 725 (CH=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, $CH_2C\underline{H}CH_2$); 4,13-4,38 m (2H, Ht-$CH_2$); 6.28-7.50 m (11H, $CH_{Ht,Ar}$);<br>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 (CH=CH of carbazole and monosubstituted benzene |
| **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 ($CH_{alk}$); 2552 (SH); 1618, 1590, (C=C, C–N); 750, 722, 690 (CH=CH of carbazole and monosubstituted benzene) |
| **13** | 1.70-3.08 m, 2.98 s (6H, $CHCH_2NCH_3$); 3.08-3.90 m (5H, $SCH_2CHCH_2$);<br>4.08-4.60 m (2H, Ht-$CH_2$); 5.15-7.63 m (11H $CH_{Ht,Ar}$);<br>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 ($CH_{alk}$); 1625, 1595, (C=C, C–N); 755, 725, 698 (CH=CH of carbazole and monosubstituted benzene) |
| **14** | 3.33 (2H, ABX system, $CH_2NPh$, $J_{AB}$ = 11 Hz, $J_{AX}$ = 3 Hz, $J_{BX}$ = 5 Hz, $H_{trans}$ and $H_{cis}$); 3.73-4.08 m (1H, $CH_2C\underline{H}CH_2$); 4.08-4.78 m (4H, Ht-$CH_2$, $SCH_2N$); 6.48-7.63 m (11H $CH_{Ht,Ar}$); 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 ($CH_{alk}$); 1596, (C=C, C–N); 748, 726, 690 (CH=CH of carbazole and monosubstituted benzene) |
| **15** | 1.19 s; 1.69 s (6H, $CH_3$); 3.25 (2H, ABX system, $CH_2NPh$, $J_{AB}$ = 10 Hz, $J_{AX}$ = 5 Hz, $J_{BX}$ = 3 Hz, $H_{trans}$ and $H_{cis}$); 3.49-3.74 m (1H, $CH_2C\underline{H}CH_2$);<br>4.35 (2H, $A^1B^1X$ system, Ht-$CH_2$, $J_{A^1B^1}$ = 15 Hz, $J_{A^1X}$ = 10 Hz, $J_{B^1X}$ = 4.5 Hz);<br>6.22-7.33 m (11H $CH_{Ht,Ar}$); 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 ($CH_{alk}$); 1620, 1590, (C=C, C–N); 755, 730, 710 (CH=CH of carbazole and monosubstituted benzene) |

TABLE 2 (continued)

| 1 | 2 | 3 | 4 |
|---|---|---|---|
| **16** | 3.65-4.00 m (2H, $CHC\underline{H}_2N$–Ar); 4.00-4.65 m (3H, Ht-$CH_2CH$);<br>6.13 s (1H, ArCH); 6.35–7.90 m (16H, $CH_{Ht,Ar}$);<br>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, $C\underline{H}_3CH_2$, $J$ = 7 Hz); 3.19, 3.29 two quartets (4H, $C\underline{H}_3C\underline{H}_2$, $J$ = 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 $CH_{Ht,Ar}$); 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 *p*-substituted benzene); 744, 724, 692 (CH=CH of carbazole and monosubstituted benzene) |
| **18** | 3.48–3.90 m (2H, $CHC\underline{H}_2N$-Ar); 3.90-4.65 m (4H, Ht-$CH_2CH$, SCHN);<br>6.04-6.29 m (3H, CH of furan); 6.58-7.56 m (11 H, $CH_{Ht,Ar}$);<br>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, $CH_2NPh$, $J_{AB}$ = 10 Hz, $J_{AX}$ = 10 Hz, $J_{BX}$ = 6 Hz, $H_{trans}$ and $H_{cis}$); 3.84-4.14 m (1H, $CH_2C\underline{H}CH_2$); 4.14-4.88 m (2H, Ht-$CH_2$); 4.41 s (2H, $SCH_2N$); 6.46-7.75 m (10H, $CH_{Ht,Ar}$); 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 *p*-disubstituted benzene); 755, 725, (CH=CH of carbazole) |
| **20** | 3.35 (2H, ABX system, $CH_2NPh$, $J_{AB}$ = 10 Hz, $J_{AX}$ = 2 Hz, $J_{BX}$ = 5 Hz, $H_{trans}$ and $H_{cis}$); 3.75-4.11 m (1H, $CH_2C\underline{H}CH_2$); 4.11-4.81 m (2H, Ht-$CH_2$);<br>4.34 s (2H, $SCH_2N$); 6.29-7.75 m (10H, $CH_{Ht,Ar}$);<br>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 *m*-disubstituted benzene); 750, 725, (CH=CH of carbazole) |
| **21** | 3.06-3.94 m (6H, $CHCH_2NAr$); 3.94-4.69 m (8H, Ht–$CH_2$, $ArCH_2N$);<br>6.06-7.69 m (32H, $CH_{Ht,Ar}$); 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) |

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 the mixtures obtained by the action of 4-fluoroaniline and also 3-chloroaniline on ETPC with an excess of formalin. The reaction of propanethiol **1** with acetone was initiated by sunlight and did not take place in darkness.

By disulfide **2** alkylation with benzyl chloride the dibenzylated derivative, 3,3'-bis(benzylphenylamino)-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 comparatively good photosensitivity ($S_{445}$ = 30, $S_{125}$ = 24 $m^2$/J) and good physicomechanical properties.

## EXPERIMENTAL

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

**Synthesis of 3,3'-Bis(R-phenylamino)-1,1'-bis(carbazol-9-yl)diprop-2-yl Disulfide** (**2-9**). A mixture of ETPC (0.01 mol), aromatic amine (0.05 mol) (ratio 1:5), and toluene (25 ml) was kept at room temperature (method A) or was heated at temperature 105-110°C (method B). The mixture was washed with 10% solution of HCl to remove the excess of aromatic amine, toluene was distilled off, 25% $H_2O_2$ (1-1.5 ml) and 0.2N NaOH (20 ml) 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-1,1'-bis(carbazol-9-yl)diprop-2-yl disulfide (**2**) (18%) were obtained.

**3,3'-Bis(1-naphthylamino)-1,1'-bis(carbazol-9-yl)diprop-2-yl Disulfide** (**10**). ETPC (2.4 g , 0.01 mol) was dissolved in toluene (25 ml), 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, and the precipitate of **10** was filtered off and washed with ethanol.

**1-(Carbazol-9-yl)-3-(N-methylphenylamino)-2-propanethiol (11) and 3-(N-Ethylphenylamino-1-(carbazol-9-yl)-2-propanethiol (12).** ETPC (9.6 g, 0.04 mol) was dissolved in toluene (40 ml), 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, 2:2:21 system). The mixture was washed with 60 ml of 10% hydrochloric acid, toluene was distilled off, and precipitates of compounds **11**, **12** filtered off and washed with 2-propanol.

**1,2-Epoxy-5-(carbazolyl-9-methyl)-6-(N-methylphenylamino)-4-thiahexane (13).** A mixture of compound **11** (3.5 g, 0.01 mol), CEP (15 ml), 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).** 40% Formalin (9 ml, 0.1 mol) was added to a solution of compound **1** (3.3 g, 0.01 mol) in $CHCl_3$ (30 ml), and the mixture was stirred for 0.5 h at room temperature (TLC control, eluent diethyl ether–hexane, 1:4). Then formalin was separated, chloroform evaporated, and the precipitate filtered off, and the 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 acetone (30 ml) was kept at room temperature in sunlight (TLC control, eluent acetone–hexane, 1:4). The precipitate of compound **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 $CHCl_3$ (30 ml) benzaldehyde (5.3 g , 0.05 mol) was added, and the mixture was kept for 2 h at room temperature (TLC control, eluent diethyl ether–hexane, 1:2). Then the mixture was treated with $NaHCO_3$ solution, chloroform was distilled off, and the 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) and $K_2CO_3$ (2 g) were added to a solution of compound **1** (3.3 g, 0.01 mol) in toluene (30 ml), and the mixture was stirred for 24 h at room temperature (TLC control, eluent diethyl ether–hexane, 1:2). Then the mixture was washed with water, toluene was distilled off, and the 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 $CHCl_3$ (30 ml), and the mixture was stirred at room temperature (TLC control, eluent diethyl ether–hexane, 1:1). Trichloromethane and 2-furaldehyde excess were distilled, and the precipitate filtered off and washed with a mixture of diethyl ether and hexane (1:1).

**3-(4-Fluorophenyl)- and 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 toluene (25 ml) was heated at 100-105°C (TLC control, eluent diethyl ether–hexane, 1:2). Then the mixture was treated with 10% hydrochloric acid (14 ml), toluene was distilled off, and the precipitate of thiazolidines **19**, **20** was filtered off, dissolved in $CHCl_3$ and treated with an excess solution of 40% formalin. Compounds **19** and **20** were purified by the procedure described for **14**.

**3,3'-Bis(benzylphenylamino)-1,1'-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), $K_2CO_3$ (0.6 g, 0.005 mol), and 2-propanol (30 ml) was heated for 10 h at 80-85°C (TLC control, eluent diethyl ether–hexane, 1:2). Then the mixture extracted with toluene, toluene was distilled off, and the precipitate of **21** was filtered off and washed with ethanol.

## REFERENCES

1. G. I. Braz, *Zh. Org. Khim.*, **21**, 688 (1951).
2. R. J. Winemann, M. H. Gollis, J. C. James, and A. M. Pomponi, *J. Org. Chem.*, **27**, 4222 (1962).
3. J. M. Stewart, *J. Org. Chem.*, **28**, 596 (1963).
4. V. A. Mullin, A. I. Zolotov, and V. I. Shishkin, *Izv. Vuzov., Khim. Khim. Tekhnol.*, **23**, 41 (1980).