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REACTION OF EPOXYPROPYLCARBAZOLE DERIVATIVES WITH 2-PHENYLINDOLE

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The reactions of 9-(2,3-epoxypropyl)carbazole and the glycidyl ether of 1,3-di(9-carbazolyl)-2-propanol with 2-phenylindole were studied. The addition of the epoxypropylcarbazole derivatives to 2-phenylindole in 2-butanone in the presence of alkali at room temperature occurs at the nitrogen atom, while the addition proceeds at $C_{(3)}$ upon heating these epoxy compounds with 2-phenylindole.

Keywords: 9-(2,3-epoxypropyl)carbazole, 1,3-di(9-carbazolyl)-2-propanol glycidyl ether, 2-phenylindole, alkylation.

The discovery of the photosemiconductance of poly(vinylcarbazole) [1] has led to considerable interest in the practical applications of carbazole derivatives, especially in electrophotography [2, 3]. In previous work [4-7], we have reported the synthesis of branched carbazole photosemiconductors, which hold promise as electrophotographic record carriers. The general scheme for the synthesis of such organic photosemiconductors involving the addition of two molecules of the 1,3-di(9-carbazolyl)-2-propanol glycidyl ether (DCPGE) with various binding agents such as aniline derivatives [4], dihydroxy compounds [6, 7], or dimercapto compounds [7] yields a variety of compounds with a broad range of semiconductor properties.

In the present work, we studied the reaction of epoxypropylcarbazole derivatives with 2-phenylindole in order to utilize this indole as the connecting fragment to obtain branched carbazole photosemiconductors.

2-Phenylindole may act as either a C- or N-nucleophile in the nucleophilic opening of the oxirane ring, depending on the conditions. In basic media (in the presence of potassium hydroxide), the indolyl anion formed reacts with 9-(2,3-epoxypropyl)carbazole (**1**) as an N-nucleophile to give 1-(9-carbazolyl)-3-(2-phenyl-1-indolyl)-2-propanol (**2**), whose structure was confirmed by its conversion to the corresponding glycidyl ether **3**. We should note that **2** was also obtained in the reaction of 1-(2,3-epoxypropyl)-2-phenylindole with carbazole under the same conditions but with a lower yield.

Heating 9-(2,3-epoxypropyl)carbazole with 2-phenylindole at 190-195°C gave a compound whose melting point did not correspond to **2**. IR and ^{1}H NMR spectroscopy indicated that this compound is a 3-substituted 2-phenylindole derivative, i.e., 1-(9-carbazolyl)-3-(2-phenyl-3-indolyl)-2-propanol (**4**). The IR spectrum of **4** has a band at 3495 cm^{-1} characteristic for hydroxyl group stretching vibrations and a band at 3310 cm^{-1} for NH group stretching vibrations. The presence of an NH group is also indicated by the singlet at 11.13 ppm in the ^{1}H NMR spectrum, which lacks the signal at 6.30-6.50 ppm for 3-H in 2-phenylindole. Furthermore, the structure of **4** was supported by reaction with potassium hydroxide in xylene using azeotropic distillation of water and subsequent treatment with 1-chloro-2,3-epoxypropane as well as by its reaction with chloroepoxypropane in an organic solvent in the presence of alkali to give 1-(9-carbazolyl)-3-[1-(2,3-epoxypropyl)-2-phenyl-3-indolyl]-2-propanol (**5**), whose structure was supported by the lack stretching bands for the NH group and appearance of oxirane bands at 1230, 930, and 870 cm^{-1} and signals for an ABX system as doublets at 2.09 and 2.15 ppm with J = 2.5 Hz and a triplet at 2.48 ppm with J = 4 Hz in the ^{1}H NMR spectra. The IR band at 3540 cm^{-1} indicates the presence of a hydroxyl group and suggests that the hydrogen at the nitrogen atom rather than the hydroxyl group participates in the reaction with chloroepoxypropane.

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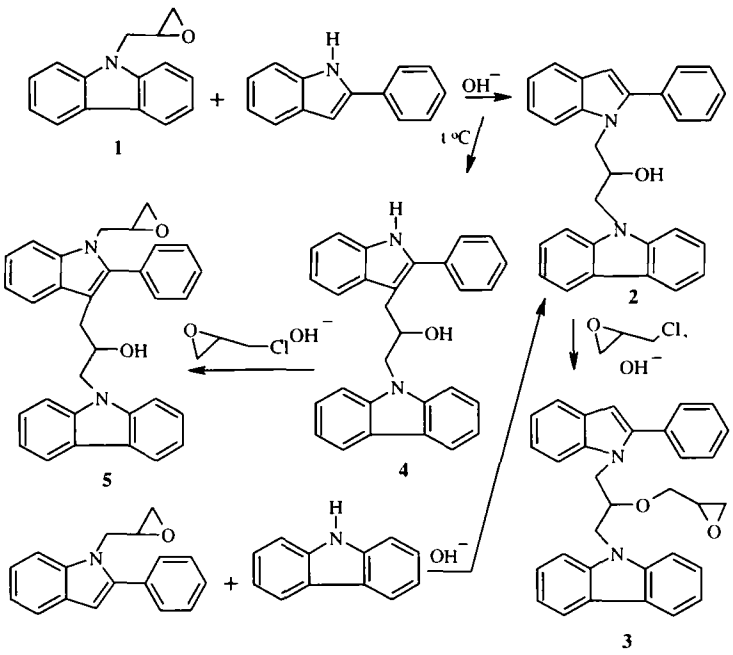
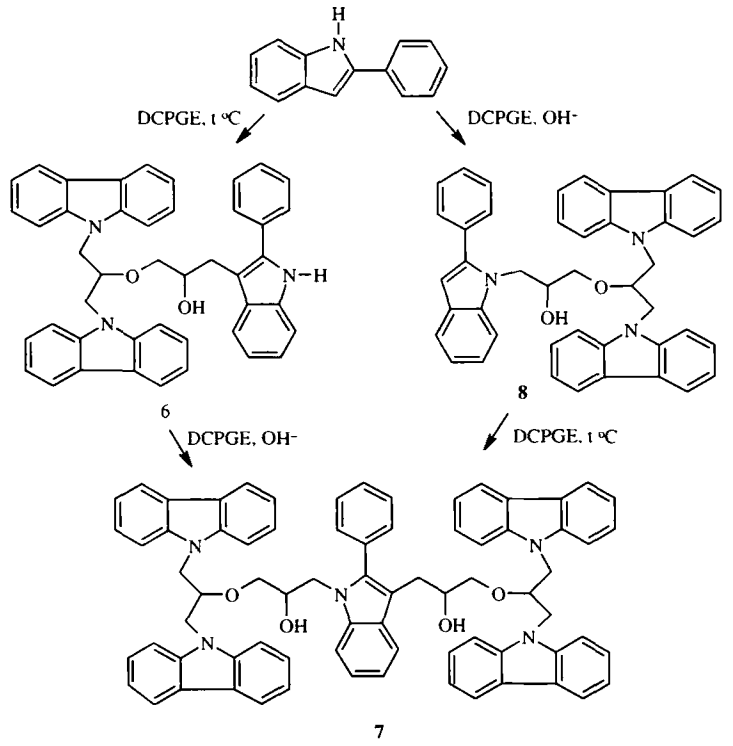


To obtain compounds with a greater number of carbazole chromophors the developed procedures were used. As expected, heating DCPGE with 2-phenylindole gives 6-(9-carbazolyl)-5-(9-carbazolylmethyl)-1-(2-phenyl-3-indolyl)-4-oxa-2-hexanol (**6**). The reaction of DCPGE and **6** in the presence of alkali gave 1,3-bis[2-hydroxy-6-(9-carbazolyl)-5-(9-carbazolylmethyl)-4-oxahexyl]-2-phenylindole (**7**), which we also obtained by the reaction of DCPGE with 2-phenylindole in the presence of alkali and subsequent heating of 6-(9-carbazolyl)-5-(9-carbazolylmethyl)-1-(2-phenyl-1-indolyl)-4-oxa-2-hexanol (**8**) and DCPGE at 210-215°C.



Thus, the synthesis of the desired product **7** was achieved both using 3-substituted 2-phenylindole **6** and N-substituted derivative **8**. The method using the N-substituted derivative holds greater promise since the formation of **8** is accomplished smoothly in high yield while isolation of the 3-substituted 2-phenylindole product requires chromatography of the crude product mixture.

EXPERIMENTAL

Starting 1-(2,3-epoxypropyl)-2-phenylindole [8] was obtained by the reaction of 2-phenylindole with chloroepoxypropane according to method [9], while the 1,3-di(9-carbazolyl)-2-propanol glycidyl ether (DCPGE) was prepared according to our earlier procedure [10]. The ^{1}H NMR spectra of **2-6** and **8** were taken on a Tesla BS-487 spectrometer at 80 MHz with HMDS as the internal standard, while the spectrum of **7** was recorded on a Bruker AC 250 spectrometer with TMS as the internal standard. The IR spectra were taken for samples in KBr pellets on a UR-20 spectrometer. The course of the reactions and purity of the products were monitored by thin-layer chromatography for **2**, **4**, **6**, and **8** on Silufol plates using toluene as the eluent and development with iodine vapor, for **3** on Silufol UV-254 plates using 1:7 acetone–hexane as the eluent, for **7** on Silufol UV-254 plates using 1:3 acetone–hexane as the eluent, and for **5** on Silufol UV-254 plates using 1:1 ether–hexane as the eluent. The spots of **3**, **5**, and **7** were found using UV light. Chemapol L 40/100 silica gel was used for column chromatography.

1-(9-Carbazolyl)-3-(2-phenyl-1-indolyl)-2-propanol (2). A. A sample of 85% powdered KOH (6.6 g, 0.1 mol) was added to a solution of 2-phenylindole (19.3 g, 0.1 mol) and 9-(2,3-epoxypropyl)carbazole (22.3 g, 0.1 mol) in 2-butanone (100 ml) and shaken vigorously for 13 h at room temperature. At the end of the reaction, 2-butanone was distilled off and the residue was treated with ether. The ethereal extracts were washed with water until the wash water was neutral. The organic layer was dried over anhydrous magnesium sulfate, treated with activated charcoal, and filtered. Ether was removed and the residue was dissolved in ethanol. The crystals formed upon standing were filtered off and washed with ethanol to give 31.0 g (74%) of compound **2**; mp 136.5-137.5°C (toluene). IR spectrum, cm^{-1}: 3543, 3460 (OH, br), 3055, 3030 (CH_{arom}), 2935, 2910, 2870 (CH_{aliph}). ^{1}H NMR spectrum ($CDCl_3$), ppm: 1.59 (1H, s, OH); 3.50-4.38 (5H, m, N–CH_2CHCH_2–N); 6.46 (1H, s, 3-H 2-phenylindole); 6.75-7.75 (15H, m, CH_{arom}); 7.93 (2H, m, 4-H, 5-H carbazole). Found, %: C 83.51; H 5.79; N 6.90. $C_{29}H_{24}N_2O$. Calculated, %: C 83.62; H 5.81; N 6.73.

B. Product **2** was obtained by the reaction of 1-(2,3-epoxypropyl)-2-phenylindole (12.5 g, 0.05 mol) and carbazole (8.4 g, 0.05 mol) in the presence of 85% powdered KOH (3.3 g, 0.05 mol) according to procedure A. The reaction time was 35 h. The product was isolated by chromatography of the reaction mixture using 1:4 acetone–hexane as the eluent. The yield of **2** was 9.8 g (47%). A sample of this product with the product obtained according to procedure A did not give a depressed melting point.

1-(9-Carbazolyl)-3-(2-phenyl-1-indolyl)-2-propanol Glycidyl Ether (3). A mixture of **2** (25.0 g, 0.06 mol), chloroepoxypropane (28 ml, 0.36 mol), 85% powdered KOH (7.9 g, 0.12 mol), and anhydrous K_2CO_3 (2.1 g, 0.015 mol) in 2-butanone (150 ml) was stirred vigorously at room temperature for 25 h. At the end of the reaction, the product was isolated by analogy to **2** (procedure A). The yield of **3** was 25.0 g (88%); mp 135.5-136.5°C (acetone). IR spectrum, cm^{-1}: 3055, 3040, 2995 (CH_{arom}), 2960, 2935, 2920, 2875 (CH_{aliph}), 1250, 920, 850 (oxirane ring vibrations). ^{1}H NMR spectrum ($CDCl_3$), ppm: 1.53-2.43 (3H, m, oxirane ring protons); 2.63 (2H, m, O–CH_2); 3.40-4.75 (5H, m, N–CH_2CHCH_2–N); 6.38-8.50 (18H, m, CH_{arom}). Found, %: C 81.34; H 6.01; N 5.85. $C_{32}H_{28}N_2O_2$. Calculated, %: C 81.33; H 5.97; N 5.93.

1-(9-Carbazolyl)-3-(2-phenyl-3-indolyl)-2-propanol (4). A mixture of 9-(2,3-epoxypropyl)carbazole (33.5 g, 0.15 mol) and 2-phenylindole (29.0 g, 0.15 mol) was heated at 190-195°C for 35 h. The product was isolated by subjecting the reaction mixture to chromatography using 1:3 ether–hexane as the eluent. After removal of the eluent, the crystalline product was filtered off and washed with ether. The yield of **4** was 22.4 g (36%); mp 201-202.5°C (toluene). IR spectrum, cm^{-1}: 3495 (OH), 3310 (NH), 3065, 3055, 3030 (CH_{arom}), 2970, 2940, 2920, 2885 (CH_{aliph}). ^{1}H NMR spectrum (DMSO-d_6), ppm: 3.08 (2H, m, 3-CH_2 2-phenylindole); 4.38 (3H, m, N–CH_2CH); 5.23 (1H, m, OH); 6.75-7.75 (15H, m, CH_{arom}); 8.0 (2H, m, 4-H, 5-H carbazole), 11.13 (1H, s, NH). Found, %: C 83.49; H 5.80; N 6.62. $C_{29}H_{24}N_2O$. Calculated, %: C 83.63; H 5.81; N 6.73.

1-(9-Carbazolyl)-3-[1-(2,3-epoxypropyl)]-2-phenyl-3-indolyl)-2-propanol (5). A. A sample of 85% powdered KOH (1.3 g, 0.02 mol) was added to a solution of compound **4** (4.2 g, 0.01 mol) in xylene (50 ml) and the mixture was heated at reflux until there was no further azeotropic distillation of water. After cooling, xylene was decanted and chloroepoxypropane (10 ml) was added. The mixture was vigorously stirred. At the end of the reaction, the mixture was diluted with toluene and washed with water until the wash water was neutral. The organic layer was dried over magnesium sulfate, treated with activated charcoal, and filtered. After removal of the solvents, the residue was purified chromatographically using 1:4 acetone–hexane as the eluent. The yield of **5** was 2.8 g (60%); mp 169-170.5°C (toluene). IR spectrum, cm^{-1}: 3540 (OH), 3050, 3005 (CH_{arom}), 2940, 2920 (CH_{aliph}), 1230, 930, 870 (oxirane ring vibrations). ^1H NMR spectrum ($CDCl_3$), ppm: 1.73 (1H, s, OH); 2.12 (1H, dd, ABX system, *trans*-H_A of oxirane ring, J_{AB} = 5.0, J_{BX} = 2.5); 2.48 (1H, t, ABX system, *cis*-H_B of oxirane ring, J_{BX} = 4.0); 2.90 (3H, m, H_X of oxirane ring and 3-CH_2 of 2-phenylindole); 4.09 (5H, m, N–CH_2C<u>H</u>(OH), N–CH_2); 6.95-7.82 (15H, m, CH_{arom}); 7.94 (2H, m, 4-H, 5-H carbazole). Found, %: C 81.25; H 5.89; N 5.78. $C_{32}H_{28}N_2O_2$. Calculated, %: C 81.33; H 5.97; N 5.93.

B. A sample of powdered KOH (2.0 g, 0.03 mol), anhydrous K_2CO_3 (0.7 g, 5 mmol), and chloroepoxyropane (5 ml) were added to a solution of compound **4** (4.2 g, 0.01 mol) in 4-butanone (30 ml) and the mixture was stirred vigorously for 4 h at room temperature. The product was isolated as in procedure A. The yield of **5** was 3.0 g (64%). A sample of this product mixed with a sample of the product obtained by procedure A did not give a depressed melting point.

6-(9-Carbazolyl)-5-(9-carbazolylmethyl)-4-oxa-1-(2-phenyl-3-indolyl)-2-hexanol (6) was obtained from DCPGE (8.9 g, 0.02 mol) and 2-phenylindole (4.0 g, 0.02 mol) and isolated by analogy to the isolation of **4**. The yield of compound **6** was 4.8 g (37%); mp 188.5-190°C (toluene). IR spectrum, cm^{-1}: 3540 with shoulder at 3520 (OH), 3255 (NH, br), 3050, 3030 (CH_{arom}), 2930, 2910, 2880, 2860 (CH_{aliph}). Found, %: C 82.05; H 5.81; N 6.53. $C_{43}H_{37}N_3O_2$. Calculated, %: C 82.27; H 5.94; N 6.69.

1,3-Bis[2-hydroxy-6-(9-carbazolyl)-5-(9-carbazolylmethyl)-4-oxahexyl]-2-phenylindole (7). A. A sample of 85% powdered KOH (0.8 g, 12 mmol) and anhydrous K_2CO_3 (0.3 g, 2 mmol) were added to a solution of **6** (2.5 g, 4 mmol) and DCPGE (1.8 g, 4 mmol) in 2-butanone (20 ml) and stirred vigorously at room temperature for 22 h. At the end of the reaction, the precipitate was filtered off and washed with water and 2-butanone. The yield of **7** was 2.8 g (65%); mp 223-224.5°C (chlorobenzene). IR spectrum, cm^{-1}: 3500 with shoulder at 3550 (OH), 3050, 3030 (CH_{arom}), 2940, 2880, 2830 (CH_{aliph}). ^1H NMR spectrum (DMF-d_7), ppm: 2.10-3.95 (12H, m, 2×O–CH_2CH(OH)CH_2 at N and C-3 2-phenylindole); 4.20-4.85 (10H, m, 2×N–CH_2CH(OH)CH_2); 6.80-7.75 (33H, m, CH_{arom}); 8.15 (8H, m, 4-H, 5-H carbazole). Found, %: C 81.71; H 5.80, N 6.57. $C_{74}H_{63}N_5O_4$. Calculated, %: C 81.82; N 5.85; N 6.45.

B. A mixture of **6** (5.0 g, 8 mmol) and DCPGE (3.6 g, 8 mmol) was heated for 50 h at 210-215°C. At the end of the reaction, the mixture was cooled to 150°C and then poured slowly into 50 ml chlorobenzene with stirring. The precipitate formed was filtered off and washed with 2-butanone. The yield of **7** was 3.2 g (37%). A sample of this product mixed with a sample of **7** obtained by procedure A did not give a depressed melting point.

6-(9-Carbazolyl)-5-(9-carbazolylmethyl)-4-oxa-1-(2-phenyl-1-indolyl)-2-hexanol (8) was obtained from DCPGE (13.4 g, 0.03 mol) and 2-phenylindole (5.8 g, 0.03 mol) in the presence of 85% powdered KOH (4.0 g, 0.06 mol) and anhydrous K_2CO_3 (2.1 g, 0.015 mol) in 2-butanone (50 ml) by analogy to procedure A for the preparation of **2**. The reaction time was 24 h. The yield of **8** was 13.9 g (72%); mp 152-153.5°C (toluene). IR spectrum, cm^{-1}: 3510 (OH), 3050, 3030 (CH_{arom}), 2950, 2920, 2880 (CH_{aliph}). ^1H NMR spectrum ($CDCl_3$), ppm: 1.85 (1H, m, OH); 2.50 (2H, m, O–CH_2); 3.35 (1H, m, O–CH_2C<u>H</u>CH_2–N); 3.50 (7H, m, CH_{arom}). Found, %: C 82.15; H 5.85; N 6.75. $C_{43}H_{37}N_3O_2$. Calculated, %: C 82.27; H 5.94; N 6.69.

REFERENCES

1. H. Hoegl, *J. Phys. Chem.*, **69**, 755 (1965).
2. P. Stroghriel and J. V. Garzulevicius, in: H. S. Nalwa (editor), *Handbook of Organic Conductive Molecules and Polymers*, John Wiley and Sons, Chichester (1997), pp. 1, 553.
3. G. V. Avilov, *Organic Electrophotographic Film* [in Russian], Isskustvo, Moscow (1985).

4. S. N. Uss, V. S. Budrene, A. A. Stanishauskaite, I. B. Sidaravichyus, A. I. Undzenas, S. A. Neduzhii, and Yu. E. Radugina, *General Questions in Radioelectronics* [in Russian], Vol. 7 (1986), p. 82.
5. S. N. Uss, V. I. Gaidyalis, A. I. Undzenas, L. A. Mikolaitene, and A. A. Stanishauskaite, in: *Abstracts of the First All-Union Conference on Polymeric Organic Semiconductors and Derived Recording Material* [in Russian], Kiev (1989), p. 70.
6. S. Uss, V. Uss, V. Budrene, A. Stanishauskaite, and S. Kutkyavichyus, *Elektrografiya 91, Abstracts of the International Conference* [in Russian], Moscow (1991), pp. 2, 119.
7. S. Kutkevicius, A. Stanisauskaite, V. Getautis, and A. Railaite, *J. Prakt. Chem.*, **337**, 315 (1995).
8. G. Buchman and K. H. Graul, *Die Pharmazie*, **1**, 21 (1971).
9. A. A. Stanishauskaite and V. M. Getautis, *Nauchn. Trudy VUZov LitSSR. Khim. Khim. Tekhnol.*, **25**, 127 (1984).
10. A. A. Stanishauskaite, V. M. Gyatautis, and L. A. Mikolaitene, Dep. in LitNII–NTI, No. 1708-Li (1986).