Chemistry of Heterocyclic Compounds, Vol. 38, No. 7, 2002

SYNTHESIS OF BRANCHED HYDRAZONES BY REACTION OF N-(2,3-EPOXYPROPYL) DERIVATIVES OF HYDRAZONES WITH BENZENEDIOLS

V. Getautis, M. Daskeviciene, A. Stanisauskaite, and O. Paliulis

A series of branched hydrazones have been prepared by reaction of N-(2,3-epoxypropyl) derivatives of 9-ethyl-3-carbazolecarbaldehyde and 4-diethylamino-benzcarbaldehyde phenylhydrazones with 1,2-, 1,3-, and 1,4-benzenediols. It was found that the reaction rate depends on the polarity of solvents.

Keywords: benzenediols, epoxypropyl derivatives, hydrazones, triethylamine, polarity of solvents.

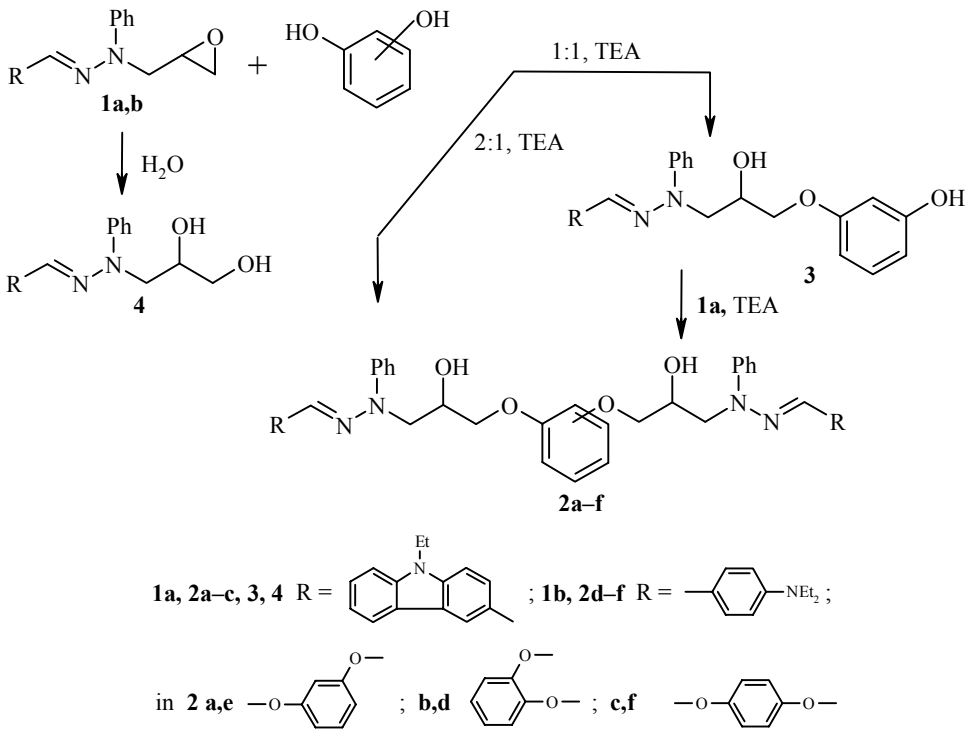
In previous works [1-4] we have reported the synthesis of branched carbazole photoconductors, which hold promise as electrophotographic record carriers. The general scheme for the synthesis of such organic photoconductors involving the addition of two molecules of the epoxypropyl carbazole derivatives with various binding agents, for example 2-phenylindole, aniline derivatives, and dihydroxy or dimercapto compounds, yields a variety of products with a broad range of semiconductor properties.

In the present work we studied the reaction of epoxypropyl derivatives, 9-ethyl-3-carbazolecarbaldehyde N-(2,3-epoxy)propyl-N-phenylhydrazone (**1a**) and 4-diethylaminobenzaldehyde N-(2,3-epoxy)propyl-N-phenylhydrazone (**1b**) with benzenediols. The aim of the study was to obtain branched hydra-zones, as hydrazones became the subject of numerous and wide investigations for application in optical and electric devices [5, 6].

The nucleophilic opening of the oxirane ring in the hydrazone **1a** according to the known method [4], i.e., by heating hydrazone **1a** with resorcinol (molar ratio 2:1) at 90-95°C in the presence of triethylamine (TEA) gave 1,3-bis[6-(9-ethylcarbazol-3-yl-methylene)-3-hydroxy-5-phenyl-5,6-diaza-1-oxahexyl]benzene (**2a**) in 40.2% yield. An insoluble resin was always found to precipitate on the bottom of the flask after the reaction performed in chlorobenzene. It was identified as a mixture of unreacted benzenediol and its monosubstituted derivative **3**. The intermediacy of the monosubstituted resorcinol was supported by the isolation of 3-[6-(9-ethylcarbazol-3-ylmethylene)-3-hydroxy-5-phenyl-5,6-diaza-1-oxahexyl]phenol (**3**) when the hydrazone epoxypropyl derivative **1a** was treated with an excess of the 1,3-benzenediol; moreover, **2a** was synthesized from **3**. The impurity of **3** could not be removed by repeated recrystallization of **2a** obtained according to the earlier described procedure, thus giving an undesirable effect on electrophotographic properties. The branched hydrazone **2a** required chromatographic purification. Obviously, chlorobenzene is not the best solvent for the reaction, because of the low solubility in it both of benzenediol itself and the intermediate product.

Kaunas University of Technology, LT-3028 Kaunas, Lithuania; e-mail: vgetaut@ctf.ktu.lt. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 884-888, July, 2002. Original article submitted January, 30, 2001.

 0009-3122/02/3807-0778$27.00



With the aim of selecting a more suitable solvent, several parallel experiments were carried out using solvents with various dipole moments: toluene, chlorobenzene, tetrahydrofuran, 2-butanone, and nitromethane. It was found that the reaction rate increases with increasing polarity of the solvents (Table 1) and the reaction proceeds most rapidly in 2-butanone (the case of nitromethane requires a separate comment). We found that the reaction should be carried out in refluxing 2-butanone. This leads to good self-stirring of the reaction mixture as well as a decrease of in reaction duration from 24 to 12 hours.

The desired replacement of 2-butanone by nitromethane, a solvent of higher polarity, was unsuccessful because of the formation of a by-product, 2-(2,3-di-hydroxypropyl)-1-(9-ethylcarbazol-3-ylmethylene)-2-phenylhydrazine (**4**). This was evidenced by the synthesis of **4** by the classical method for obtaining diols from epoxypropyl derivatives [8].

TABLE 1. Solvent Effect on the Synthesis of Branched Hydrazone **2a***

Solvent	Dipole moment,*[2] D	Reaction time, h	Isolated yield, %	Method of product isolation
Toluene	0.06	48	37.4	Column chromat.
Chlorobenzene	1.55	33	40.2	Column chromat.
Tetrahydrofuran	1.71	28	53.2	Crystallization
2-Butanone	2.84	24 (12)*[3]	65.5	Crystallization
Nitromethane	3.13	6	10.3*[4]	Column chromat.

* Reactions were carried out at 70-75°C using the following molar ratious: **1a** : 1,3-benzenediol : TEA = 2.2:1:0.5.

*[2] Dipole moments determined under the same conditions are presented [7].

*[3] At reflux temperature.

*[4] Formation of by-product **4** was observed.

Based on the developed method, by interaction of compound **1a** with 1,2- and 1,4-benzenediols and **1b** with 1,2-, 1,3-, and 1,4-benzenediols, the following branched hydrazones (65-82% yields) were synthesized: 1,2- and 1,4-bis[6-(9-ethylcarbazol-3-ylmethylene)-3-hydroxy-5-phenyl-5,6-diaza-1-oxahexyl]benzenes (**2b**,**c**) and 1,2-, 1,3-, and 1,4-bis[6-(4-diethylaminobenzylidene)-3-hydroxy-5-phenyl-5,6-diaza-1-oxahexyl]benzenes (**2d-f**).

The synthesized hydrazones **2a**,**c**,**f** are crystalline substances, while **2b**,**d**,**e** were isolated using column chromatography followed by precipitation in a large excess of hexane. Hydrazones **2b**,**d**,**e** isolated by such a procedure are amorphous solids. All our attempts to crystallize them were unsuccessful. The glass transition temperatures (T_g), established by a differential scanning calorimetric method, are above room temperature. Such low-molecular glasses can be used in electrophotographic layers without binding materials. The application and photoelectric properties of the synthesized branched hydrazones will be discussed elsewhere.

EXPERIMENTAL

2,3-Epoxypropyl derivatives of hydrazones **1a**,**b** were prepared according to our earlier procedure [9]. The ^{1}H NMR (250 MHz) spectra were taken on a Bruker AC 250 spectrometer with TMS as the internal standard. The IR spectra were taken in KBr pellets on a Bio-Rad Digilab FTS-40 spectrometer for **2a-c**,**e** and on a Specord M-80 spectrometer for **2d,f** and **3** samples. Mass spectrum was obtained on a Finnigan MAT 8500 instrument (electron energy 70 eV). Differential scanning calorimetry measurements were performed on a Perkin Elmer DSC 7 instrument at a scan rate 10 K/min. The course of the reactions and purity of the products were monitored by thin-layer chromatography on Silufol UV-254 plates, using 3:1 ether–hexane as the eluent. Aluminum oxide (Brockmann II, neutral) was used for column chromatography.

1,3-Bis[6-(9-ethylcarbazol-3-ylmethylene)-3-hydroxy-5-phenyl-5,6-diaza-1-oxahexyl]benzene (2a). A. Compound **1a** (10.0 g, 27.1 mmol) and resorcinol (1.35 g, 12.3 mmol) were dissolved in 2-butanone (15 ml), and TEA (1.9 ml, 13.5 mmol) was added. The mixture was refluxed until the 1,3-benzenediol and its monosubstituted derivative disappeared (12 h). At the end of the reaction 2-butanone and TEA were distilled off and the residue was recrystallized from toluene. Product **2a** (7.4 g, 65.5%) was filtered off and washed with 2-propanol; mp 157-158.5°C (toluene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, J (Hz): 8.08 (2H, s, 4-H Ht); 8.02 (2H, d, J = 7.6, 1-H Ht); 7.85-7.73 (4H, m, 2-H Ht, CH=N); 7.50-7.04 (17H, m, Ar); 6.93 (2H, t, J = 7.0, 4-H Ph); 6.56-6.46 (3H, m, 2-H, 3-H, 4-H *m*-Ph); 4.40-3.84 (14H, m, CH_2CHCH_2, $C\underline{H}_2CH_3$); 3.06 (2H, d, J = 4.9, OH); 1.30 (6H, t, J = 7.2, CH_3). IR spectrum, ν, cm^{-1}: 3554, 3412 (OH, br), 3044 (CH_{arom}), 2979, 2933 (CH_{aliph}), 1147 (C–O–C). Found, %: C 76.05; H 6.14; N 9.92. $C_{54}H_{52}N_6O_4$. Calculated, %: C 76.39; H 6.17; N 9.90.

B. Product **2a** was obtained by the reaction of **1a** (1.26 g, 3.4 mmol) and 1,3-benzenediol monosubstituted derivative **3** (1.5 g, 3.1 mmol) in the presence of TEA (0.2 ml, 1.4 mmol) according to procedure A. The reaction time was 11 h. The yield of **2a** was 1.6 (60.4%). A sample of this product with the product obtained according to procedure A did not give a depressed melting point.

1,2-Bis[6-(9-ethylcarbazol-3-ylmethylene)-3-hydroxy-5-phenyl-5,6-diaza-1-oxahexyl]benzene (2b) was prepared as described for **2a**, except that pyrocatechol instead of resorcinol was used. The reaction time was 10 h. The product was isolated by subjecting the reaction mixture to chromatography using propanone–hexane (1:4) as the eluent. After removal of the eluents, the 20% solution of the oily residue in toluene was poured with intensive stirring into a tenfold excess of hexane. Product **2b** (8.2 g, 72.4%) was obtained as a white powder with yellow tint. T_g 78°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, J (Hz): 8.12 (2H, s, 4-H Ht); 8.00 (2H, d, J = 7.5, 1-H Ht); 7.83 (2H, s, CH=N); 7.74 (2H, d, J = 8.5, 2-H Ht); 7.50-7.10 (16H, m, Ar); 6.87 (2H, t, J = 7.2, 4-H Ph); 6.78 (4H, s, *o*-Ph); 4.50-3.90 (16H, m, $CH_2CH(OH)CH_2$, $C\underline{H}_2CH_3$); 1.26 (6H, t, J = 6.9, CH_3). IR spectrum, ν, cm^{-1}: 3600-3300 (OH), 3058 (CH_{arom}), 2979, 2931 (CH_{aliph}), 1146 (C–O–C). Found, %: C 76.01; H 6.07; N 9.78. $C_{54}H_{52}N_6O_4$. Calculated, %: C 76.39; H 6.17; N 9.90.

1,4-Bis[6-(9-ethylcarbazol-3-ylmethylene)-3-hydroxy-5-phenyl-5,6-diaza-1-oxahexyl]ben-zene (**2c**) was prepared and isolated as described for **2a**, except that hydroquinone instead of resorcinol was used. The reaction time was 10 h. Yield of **2c** 8.5 g (75.0%); mp 210.5-212°C (dioxane). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J* (Hz): 8.29 (2H, s, 4-H Ht); 8.19 (2H, d, *J* = 7.6, 1-H Ht); 8.09 (2H, s, CH=N); 7.92 (2H, d, *J* = 8.9, 2-H Ht); 7.65-7.50 (8H, m, Ar); 7.44 (2H, t, *J* = 7.2, 6-H Ht); 7.34 (4H, t, *J* = 8.2, 3-H, 5-H Ph); 7.24 (2H, t, *J* = 7.2, 7-H Ht); 7.05 (4H, s, *p*-Ph); 6.89 (2H, t, *J* = 7.6, 4-H Ph); 5.58 (2H, br. s, OH); 4.45-3.95 (14H, m, CH_2CHCH_2, $C\underline{H}_2CH_3$); 1.29 (6H, t, *J* = 6.9, CH_3). IR spectrum, ν, cm^{-1}: 3600-3350 (OH), 3044 (CH_{arom}), 2980-2820 (CH_{aliph}), 1150, 1100 (C–O–C). Found, %: C 76.07; H 6.00; N 9.82. $C_{54}H_{52}N_6O_4$. Calculated, %: C 76.39; H 6.17; N 9.90.

1,2-Bis[6-(4-diethylaminobenzylidene)-3-hydroxy-5-phenyl-5,6-diaza-1-oxahexyl]benzene (2d) was prepared and isolated as described for **2b**, except that instead of **1a** 8.8 g (27.1 mmol) of **1b** were used. The reaction time was 13 h. Yield of **2d** 7.6 g (81.7%). T_g 46°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 7.66 (2H, s, CH=N); 7.49 (4H, d, *J* = 8.8, *p*-Ph); 7.41-7.21 (8H, m, 2-H, 3-H Ph); 6.93 (4H, s, *o*-Ph); 6.92 (2H, t, *J* = 7.4, 4-H Ph); 6.63 (4H, d, *J* = 7.4, *p*-Ph); 4.46-4.31 (2H, m, C<u>H</u>OH); 4.21-3.91 (8H, m, $NC\underline{H}_2CH(O\underline{H})$, one of the CH_2O protons); 3.78 (2H, dd, *J* = 5.6, *J* = 5.6, next of the CH_2O protons); 3.37 (4H, q, *J* = 7.4, $C\underline{H}_2CH_3$); 1.17 (6H, t, *J* = 7.4, CH_3). IR spectrum, ν, cm^{-1}: 3630-3150 (OH), 3120-3000 (CH_{arom}), 2980, 2945, 2900, 2880 (CH_{aliph}), 1145 (C–O–C). Found, %: C 72.82; H 7.38; N 11.05. $C_{46}H_{56}N_6O_4$. Calculated, %: C 72.99; H 7.46; N 11.10.

1,3-Bis[6-(4-diethylaminobenzylidene)-3-hydroxy-5-phenyl-5,6-diaza-1-oxahexyl]benzene (2e) was obtained as described for **2d**, except that resorcinol instead of pyrocatechol was used. The reaction time was 14 h. Yield 6.8 g (73.1%); T_g 51°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 7.62 (2H, s, CH=N); 7.50-7.10 (14H, m, Ar); 6.91 (2H, t, *J* = 7.2, 4-H Ph); 6.70-6.50 (6H, m, 2-H, 4-H *m*-Ph, Ar); 4.38 (2H, m, C<u>H</u>OH); 4.20-3.90 (8H, m, NCH_2, CH_2O); 3.35 (8H, q, *J* = 7.4, $C\underline{H}_2CH_3$); 3.10 (2H, br s, OH); 1.16 (12H, t, *J* = 7.4 Hz, CH_3). IR spectrum, ν, cm^{-1}: 3650-3130 (OH), 3100-3000 (CH_{arom}), 2965, 2921, 2891, 2862 (CH_{aliph}), 1173, 1140 (C–O–C). Found, %: C 72.82; H 7.40; N 11.01. $C_{46}H_{56}N_6O_4$. Calculated, %: C 72.99; H 7.46; N 11.10.

1,4-Bis[6-(4-diethylaminobenzylidene)-3-hydroxy-5-phenyl-5,6-diaza-1-oxahexyl]benzene (2f) was obtained and isolated as described for **2d**, except that hydroquinone instead of pyrocatechol was used. The reaction time was 10 h. After removal of the eluents, the residue was crystallized from toluene. 7.1 g (76.3%) of **2f** was filtered off and washed with 2-propanol; mp 154-156°C (2-propanol–toluene, 1:2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 7.66 (2H, s, CH=N); 7.46 (4H, d, *J* = 8.8, *p*-Ph); 7.45-7.28 (8H, m, 2-H, 3-H, 5-H, 6-H Ph); 6.95 (2H, t, *J* = 7.4, 4-H Ph); 6.86 (4H, s, *p*-Ph); 6.65 (4H, d, *J* = 8.8, Ph); 4.39 (2H, p, *J* = 5.1, C<u>H</u>OH); 4.20-3.92 (8H, m, NCH_2, CH_2O); 3.38 (8H, q, *J* = 7.4, $C\underline{H}_2CH_3$); 3.07 (2H, d, *J* = 5.1, OH); 1.17 (12H, t, *J* = 7.0, CH_3). IR spectrum, ν, cm^{-1}: 3620-3150 (OH), 3120-3000 (CH_{arom}), 2985, 2945, 2905, 2875 (CH_{aliph}), 1150, 1110 (C–O–C). Found, %: C 72.80; H 7.39; N 10.98. $C_{46}H_{56}N_6O_4$. Calculated, %: C 72.99; H 7.46; N 11.10.

3-[6-(9-Ethylcarbazol-3-ylmethylene)-3-hydroxy-5-phenyl-5-diaza-1-oxahexyl]phenol (3). Hydrazone **1a** (3.7 g, 10 mmol) and resorcinol (11 g, 100 mmol) were dissolved in 2-butanone (20 ml), and TEA (0.7 ml, 5 mmol) was added. The mixture was refluxed until **1a** disappeared (8 h). At the end of the reaction 2-butanone and TEA were distilled off and the residue was treated with toluene. The toluene extract was washed with water until the 1,3-benzenediol disappeared in the wash water. The organic layer was dried over anhydrous magnesium sulfate, treated with activated charcoal, and filtered. Toluene was removed and the product was isolated by chromatography of the residue using propanone–hexane (1:4) as the eluent. Yield of **3** 2.2 g (45.8%); mp 160-161°C (toluene). IR spectrum, ν, cm^{-1}: 3350 (OH, br), 3075, 3030 (CH_{arom}), 2980, 2948, 2900 (CH_{aliph}), 1150 (C–O–C). Found, %: C 74.98; H 5.92; N 8.63. $C_{30}H_{29}N_3O_3$. Calculated, %: C 75.13; H 6.09; N 8.76.

2-(2,3-Dihydroxypropyl)-1-(9-ethylcarbazol-3-methylene)-2-phenylhydrazine (4). Hydrazone **1a** (10.0 g, 27.1 mmol) was dissolved in dioxane (30 ml), and 85% trifluoroacetic acid (5 ml) was added. The reaction mixture was refluxed until **1a** disappeared (2.5 h), concentrated, diluted with 1,2-dichloroethane

(100 ml), washed with water until pH 7, dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was subjected to chromatography (propanone–hexane, 1:3) to afford 5.2 g (49.5%) of **4**; mp 130-131.3°C (propanone–toluene, 1:10). Mass spectrum, *m/z* (*I*, %): 387 (M^+, 100), 326 (35), 234 (64), 221 (75), 205 (15), 194 (31), 179 (23), 106 (20), 77 (8). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 8.25 (1H, s, 4-H Ht); 8.10 (2H, d, *J* = 7.9, 1-H Ht); 7.85 (1H, s, CH=N); 7.84 (1H, d, *J* = 8.6, 2-H Ht); 7.48-7.17 (8H, m, Ar); 7.00 (1H, t, *J* = 7.0, 4-H Ph); 4.30 (2H, q, *J* = 7.2, $C\underline{H}_2CH_3$); 4.18 (1H, m, $C\underline{H}OH$); 3.96 (2H, d, *J* = 6.5, NCH_2); 3.80 (1H, dd, part of the ABX system, *cis*-H_A of CH_2O, J_{AB} = 11.5, J_{AX} = 4.0); 3.64 (1H, dd, part of the ABX system, *trans*-H_B of CH_2O, J_{BX} = 5.2); 3.2 (1H, br s, $CHO\underline{H}$); 2.45 (1H, s, $CH_2O\underline{H}$); 1.39 (3H, t, *J* = 7.2, CH_3). IR spectrum, ν, cm^{-1}: 3600-3200 (OH), 3054 (CH_{arom}), 2975, 2933 (CH_{aliph}), 1142 (C–O–C). Found, %: C 74.28; H 6.48; N 10.72. $C_{24}H_{25}N_3O_2$. Calculated, %: C 74.40; H 6.50; N 10.84.

REFERENCES

1. V. Getautis, M. Daskeviciene, and A. Stanisauskaite, *Khim. Geterotsikl. Soedin.*, 898 (2000).
2. V. Getautis, A. Stanisauskaite, and M. Daskeviciene, in: *Abstracts of 13th International Conference on Organic Synthesis*, Warsaw, Poland (2000), p. 336.
3. V. Getautis, A. Stanisauskaite, M. Daskeviciene, J. Antulis, V. Jankauskas, and E. Montrimas, in: *Abstracts of International Conference on Organic Synthesis*, Vilnius, Lithuania (2000), p. 46.
4. S. Kutkevicius, A. Stanisauskaite, V. Getautis, and A. Railaite, *J. Prakt. Chem*., **337**, 315 (1995).
5. P. Stroghriel and J. V. Grazulevicius, in: H. S. Nalwa (Ed.), *Handbook of Organic Conductive Molecules and Polymers*, John Wiley and Sons, Chichester (1997), Vol. 1, 553.
6. K. Nishimura, H. Inada, T. Kobata, Y. Matsui and Y. Shirota, *Mol. Cryst. Liq. Cryst*. *Sci. Tehnol.*, A**217,** 235 (1992).
7. O. A. Osipov, V. I. Minkin, and Yu. B. Kletenik, *Handbook of Dipole Moments* [in Russian], Rostov-on-Don State University, Rostov-on-Don, 1961.
8. I. P. Zherebtsov, V. P. Lopatinskiy, and N. M. Rovkina, USSR Inventor's Certificate 529159; *Byull. Izobret*., **53**, No. 35, 58 (1976).
9. A. Stanisauskaite, V. Getautis, and A. Railaite, *Chemija,* No. 3, 68 (1996).