The Preparation of Some Tetradecyl-Substituted Benzocarbazoles and Benzacridines

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The preparations are described of 10-dodecyl- and 10-tetradecylbenzo[*a*]acridines, 9-tetradecylbenzo[*c*]acridine, and some 8-tetradecylbenzo[*a*]carbazoles and 10-tetradecylbenzo[*c*]carbazoles.

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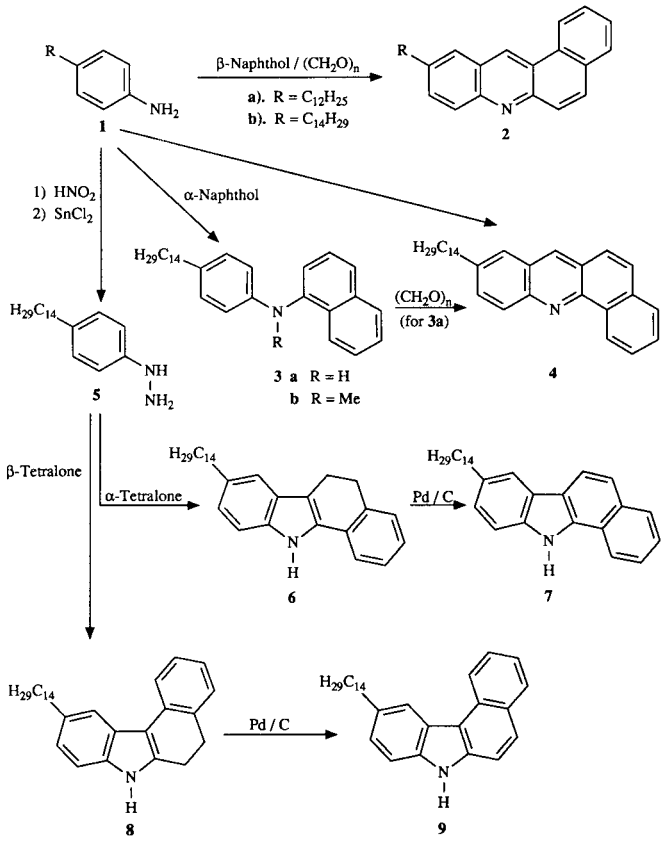
Heavy ends of natural oils contain numerous condensed heterocyclic nitrogen compounds such as benzocarbazoles and benzacridines. It has been postulated that the attractions between such components are responsible for viscosity increases and volatility decreases. Investigation of these interactions has been hindered by the poor solubility of available compounds. We have prepared some benzacridines and benzocarbazoles with C_{12} and C_{14} alkyl side chains in the hope of increasing their solubility in hydrocarbon solvents.

Synthesis.

The benz[*a*]acridines **2** were prepared directly from the appropriate 4-alkylanilines **1** by the Ullmann-Fetvadjian reaction with 2-naphthol and formaldehyde, using the method of Buu-Hoi and co-workers [1]. 1-Naphthol and **1b** condensed readily to form the substituted *N*-phenyl-1-naphthylamine **3a**, but an attempted one-pot cyclization with formaldehyde resulted in the formation of a tarry residue which contained only a small amount of the desired material. Therefore the amine was isolated and condensed with formaldehyde at elevated temperature to give the benz[*c*]acridine **4**. During the column chromatography of this product, a small first fraction was obtained which proved to be the *N*-methylated derivative **3b** of **3a**. The added methyl group appeared at δ 3.33 in the proton nmr spectrum and at δ 40.36 in the carbon spectrum (confirmed by the APT spectrum). Clearly, the formaldehyde had methylated the secondary amine to give this by-product.

The key intermediate for the preparation of the benzocarbazoles, 4-tetradecylphenylhydrazine **5**, was prepared from commerically available 4-tetradecylaniline **1b**. The hydrazine **5** was converted by Fisher indole synthesis [2,3,4] with α-tetralone into the dihydrobenzo[*a*]carbazole **6** and with β-tetralone into the dihydrobenzo[*c*]carbazole **8**. These dihydrobenzocarbazoles were dehydrogenated by palladised carbon [4,5] to the fully aromatic benzocarbazoles **7** and **9** respectively.

Scheme



NMR Spectra.

Both the proton and carbon spectra for each new compound were as expected for the required structures, see Experimental. The carbazole spectra, all measured in DMSO-d_6, showed the N-H chemical shifts at 11-12 ppm. The ring methylene protons of compounds **6** and **8** appeared as four proton singlets at *ca.* 2.9 ppm and their carbon signals were in the 18-29 ppm region. Upon dehydrogenation, all these signals moved into the respective aromatic regions, as expected.

EXPERIMENTAL

Methods.

Melting points were taken on a Thomas-Hoover melting point

apparatus equipped with a microscope and are uncorrected. The ^{1}H nmr spectra were recorded on a Varian EM-360 (60 MHz) nmr spectrometer. The ^{13}C nmr spectra were recorded on a JEOL FX-100 (25 MHz) using 5 mm tubes. Solute concentrations were 80-150 mg/ml with either deuteriochloroform or DMSO-d_6 (as stated) as the internal lock and TMS as internal reference. The ir spectra were recorded on a Perkin Elmer 283B infrared spectrophotometer. Commercially available reagent grade solvents and reagents were used without further purification.

10-Dodecylbenz[*a*]acridine **2a**.

To a boiling mixture (*ca.* 285°) of 4-dodecylaniline (2.66 g, 18.2 mmoles) and 2-naphthol (4.72 g, 17.5 mmoles), paraformaldehyde (0.65 g, 18.7 mmoles) was added in small portions. After evolution of water ceased, the mixture was heated at the same temperature for 1 minute further. The black resinous residue was boiled with ethanol (150 ml), and the resulting orange solution was decanted from a black oil which settled out. The ethanol solution was treated with picric acid (10 g, damp) and the resulting picrate was collected by vacuum filtration. Treatment of the picrate with aqueous ammonia solution gave 4.85 g of a brown solid which was purified by column chromatography (silica eluted with benzene followed by chloroform) to give 2.55 g (37%) of the acridine **2**, mp 85-86°. Under ultraviolet irradiation a strong green fluorescence was observed; ir (bromoform): 2910, 2840, 820 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 9.19 (s, 1H, H12), 8.62 (d, 1H, J = 7.8 Hz, H6), 8.16 (d, 1H, J = 9.0 Hz, H8), 7.96 (d, 1H, J = 9.3 Hz, H9), 7.86-7.54 (m, 6H, H1-5 and H11), 2.79 (t, 2H, J = 7.5 Hz, CH_2), 1.74-1.24 (m, 20H, $C_{10}H_{20}$), 0.87 (t, 3H, J = 6.6 Hz, CH_3); ^{13}C nmr (deuteriochloroform): 14.12, 22.69, 29.36, 29.54, 29.61, 29.65, 31.02, 31.92, 36.03, 122.73, 124.03, 125.94, 126.51, 127.20, 127.44, 128.42, 128.69, 129.59, 129.95, 131.18, 131.84, 132.03, 140.71, 147.13, 148.61.

Anal. Calcd. for $C_{31}H_{39}N$: C, 87.60; H, 8.87; N, 3.52. Found: C, 87.58; H, 8.96; N, 3.61.

10-(Tetradecyl)benz[*a*]acridine **2b**.

The same procedure gave the acridine **2b** (12%) mp 86-88°. Under ultraviolet irradiation a strong green fluorescence was observed; ir (bromoform): 2920, 2840, 825 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 9.22 (s, 1H, H12), 8.64 (d, 1H, J = 7.8 Hz, H6), 8.16 (d, 1H, J = 8.7 Hz, H8), 7.97 (d, 1H, J = 9.0 Hz, H9), 7.88-7.58 (m, 6H, H1-5 and H11), 2.80 (t, 2H, J = 7.6 Hz, CH_2), 1.75-1.22 (m, 24H, $C_{12}H_{24}$), 0.87 (t, 3H, J = 6.3 Hz, CH_3); ^{13}C nmr (deuteriochloroform): 14.12, 22.69, 29.37, 29.54, 29.61, 29.67, 29.68, 31.04, 31.92, 36.04, 122.75, 124.05, 125.96, 126.53, 127.22, 127.45, 128.45, 128.71, 129.60, 129.97, 131.20, 131.85, 132.04, 140.73, 147.16, 148.64.

Anal. Calcd. for $C_{31}H_{39}N$: C, 87.47; H, 9.24; N, 3.29. Found: C, 87.50; H, 9.42; N, 3.23.

N-(4-Tetradecylphenyl)-1-naphthylamine **3**.

A mixture of 4-tetradecylaniline (5.32 g, 36.5 mmoles), 1-naphthol (11.99 g, 40.2 mmoles) and iodine (0.14 g, 0.55 mmoles) was heated at 220° for 15 hours. The product was purified by column chromatography (benzene/hexane, 1:1), followed by recrystallization from ethanol to give 4.36 g (29%) of **3a**, mp 51-52°; ^{1}H nmr (deuteriochloroform): δ 7.96 (d, 1H, J = 7.5 Hz, H4), 7.81 (d, 1H, J = 6.9 Hz, H1), 7.5-7.2 (m, 5H), 7.06 (d, 2H, J = 8.5 Hz, H7 and H9). 6.92 (d, 2H, J = 8.5 Hz, H6 and H10), 5.83 (s, 1H, NH), 2.54 (t, 2H, J = 7.5 Hz, CH_2), 1.6-1.2 (m, 24H, $C_{12}H_{24}$), 0.88 (t, 3H, 6.6 Hz, CH_3); ^{13}C nmr (deuteriochloroform): 14.13, 22.70, 29.13, 29.16, 29.21, 29.37, 29.57, 29.64, 29.67, 29.70, 29.94, 29.99, 31.71, 31.94, 35.26, 114.22, 118.42, 121.51, 122.11, 125.50, 125.93, 126.02, 127.03, 128.52, 129.21, 134.66, 135.80, 139.43, 141.79.

Anal. Calcd. for $C_{30}H_{41}N$: C, 86.69; H, 9.94; N, 3.37. Found: C, 86.57; H, 10.12; N, 3.29.

9-Tetradecylbenz[*c*]acridine **4**.

N-(4-Tetradecylphenyl)-1-naphthylamine **6** (1.5 g, 3.6 mmoles) was stirred and heated to 290°. Paraformaldehyde (4.0 g, 134 mmoles) was cautiously added to this in small portions. The reaction mixture was maintained at 290° for 10 minutes further and allowed to cool to room temperature. The resulting black oil was purified by column chromatography (benzene/hexane, 1:2) to give as fraction 1, 0.11 g of a compound determined to be *N*-methyl-*N*-(4-tetradecylphenyl)-1-naphthylamine **3b**; ^{1}H nmr (deuteriochloroform): 7.86 (m, 2H), 7.71 (d, 1H, J = 8.2 Hz), 7.40 (m, 4H), 6.95 (d, 2H, J = 8.7 Hz), 6.57 (d, 2H, J = 8.7 Hz), 3.33 (s, 3H, NCH_3), 2.47 (t, 2H, J = 7.6 Hz, CH_2), 1.25 (m, 24H), 0.87 (t, 3H, J = 6.7 Hz, CH_3); ^{13}C nmr (deuteriochloroform): 14.13, 22.70, 29.38, 29.40, 29.50, 29.58, 29.65, 29.70, 31.79, 31.94, 34.99, 40.36, 113.85, 123.92, 124.78, 126.09, 126.15, 126.24, 126.35, 128.35, 128.74, 131.35, 131.79, 135.07, 145.88, 148.21. The required compound **4** was fraction 2, 0.43 g (32%) mp 44-45°. Under ultraviolet irradiation a strong green fluorescence was obeserved for **4**; ir (bromoform): 2920, 2850, 810, 800 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 9.48 (d, 1H, J = 7.8 Hz), 8.38 (s, 1H), 8.25 (d, 1H, J = 8.7 Hz), 7.79-7.58 (m, 7H), 2.76 (t, 2H, J = 7.8 Hz, CH_2), 1.70-1.18 (m, 24H, $C_{12}H_{24}$), 0.87 (t, 3H, J = 6.6 Hz, CH_3); ^{13}C nmr (deuteriochloroform): nmr 14.13, 22.70, 29.38, 29.51, 29.62, 29.71, 31.03, 31.93, 36.02, 124.99, 125.10, 125.43, 125.73, 127.01, 127.06, 127.26, 127.76, 128.65, 129.42, 131.54, 131.68, 133.72, 134.09, 140.49, 146.69, 147.00; hrms: M$^+$ Calcd. 425.3082. Found: 425.3093.

4-Tetradecylphenylhydrazine Hydrochloride **5**.

Sodium nitrite (4.8 g, 69 mmoles) in water (20 ml) was added over 15 minutes to a stirred ice-cold suspension of 4-tetradecylaniline (20 g, 67 mmoles) in 6 *M* hydrochloric acid (80 ml). After an additional 30 minutes in the ice bath, stannous chloride (44.5 g, 0.193 mole) in 6 *M* hydrochloric acid (80 ml) was added slowly and the resulting suspension was stirred at 0° for 4 hours. The resulting solid was filtered off and dissolved in a mixture of 40% potassium hydroxide solution (100 ml) and ethyl acetate (100 ml). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 x 100 ml). The combined organic extracts were shaken with 10% hydrochloric acid (50 ml) whereupon a colorless solid formed in the organic layer. The crude product was filtered off and recrystallized from ethanol to give 16.1 g (70%) of **5** as white mircrocrystals, mp 153-155°; ir (bromoform): 2920, 2840, 1470, 710 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 10.48 (m, 4H, $NHNH_3^+$), 7.45-6.78 (m, 4H, aromatic protons), 2.18 (t, 2H, J = 7.0 Hz, CH_2), 2.78-1.02 (m, 24H, $C_{12}H_{24}$), 0.84 (t, 3H, J = 4 Hz, CH_3); ^{13}C nmr (DMSO-d_6): 13.57, 21.77, 28.34, 28.68, 30.78, 30.97, 34.09, 114.85, 128.35, 135.46, 143.07.

Anal. Calcd. for $C_{20}H_{37}ClN_2$: C, 70.45; H, 10.94; N, 8.22. Found: C, 70.46, H, 11.10; N, 8.02.

5,6-Dihydro-8-tetradecyl-11-*H*-benzo[*a*]carbazole **6**.

A stirred suspension of 4-tetradecylphenylhydrazine hydro-

chloride (93.0 g, 8.8 mmoles) in concentrated hydrochloric acid (4 ml) and water (43 ml) was heated at 80° for 2 minutes while α-tetralone (1.29 g, 8.8 mmole) was added dropwise. The mixture was stirred and refluxed for 4.5 hours, cooled, and allowed to stand overnight. The white precipitate which formed was filtered off, washed with water (10 ml) and dried at 60° *in vacuo*. The mother liquor was concentrated to 30% of its original volume and a second crop was collected. The combined crude product was recrystallized from ethanol to give 2.3 g (63%) of **6** as white plates, mp 107-109°; ir (bromoform): 3380, 2905, 2840, 800, 755, 750, 710 cm^{-1}; ^1H nmr (DMSO-d_6): δ 11.43 (s, 1H, NH), 7.87-6.87 (m, 7H, aromatic protons), 2.93 (s, 4H, ring C_2H_4), 2.63 (t, 2H, J = 6.0 Hz, CH_2), 1.7-1.0 (m, 24H, $C_{12}H_{24}$), 0.84 (t, 3H, J = 4.0 Hz, CH_3); ^{13}C nmr (DMSO-d_6): 6.31, 6.41, 13.04, 18.86, 21.32, 28.00, 28.14, 28.34, 28.54, 30.63, 30.92, 34.92, 109.97, 110.41, 116.60, 120.21, 121.92, 125.57, 125.86, 127.42, 128.84, 132.25, 135.22, 135.51.

Anal. Calcd. for $C_{30}H_{41}N$: C, 86.69; H, 9.94; N, 3.37. Found: C, 86.59; H, 10.02; N, 3.11.

8-Tetradecyl-11-*H*-benzo[*a*]carbazole **7**.

A mixture of dihydrobenzo[*a*]carbazole **6** (1.04 g, 2.5 mmoles) and 5% palladised carbon (0.11 g) was heated in a sand bath at 250-260° for 30 minutes. The reaction mixture was cooled and extracted with hot benzene (40 ml). The extract was filtered and concentrated under reduced pressure to give the crude product. This was recrystallized from methanol/benzene (1:1) to give 0.89 g (86%) of **7** as white plates, mp 154-156°; ir (bromoform): 3430, 2910, 2840, 810, 800 cm^{-1}; ^1H nmr (DMSO-d_6): δ 12.25 (s, 1H, NH), 8.82-7.18 (m, 9H, aromatic protons), 2.79 (t, 2H, J = 7.0 Hz, CH_2), 2.59-1.00 (m, 24H, $C_{12}H_{24}$), 0.84 (t, 3H, J = 4.0 Hz, CH_3); ^{13}C nmr (DMSO-d_6): 13.13, 21.37, 28.00, 28.14, 28.39, 30.68, 31.02, 34.92, 110.51, 116.90, 118.07, 118.31, 118.75, 121.23, 123.04, 124.35, 124.69, 127.86, 131.52, 132.69, 135.12, 136.98.

Anal. Calcd. for $C_{30}H_{39}N$: C, 87.11; H, 9.50; N, 3.39. Found: C, 87.23; H, 9.63; N, 3.35.

5,6-Dihydro-10-tetradecyl-7-*H*-benzo[*c*]carbazole **8**.

A stirred solution of 4-tetradecylphenylhydrazine hydrochloride (15 g, 8.8 mmoles) in concentrated hydrochloric acid (20 ml) and water (215 ml) was heated to 40°. Over a period of 10 minutes, β-tetralone (6.45 g, 8.8 mmoles) was added dropwise, then the solution was warmed to 65° and maintained there for 1.5 hours. After cooling the precipitate which formed was filtered off and dried over phosphorus pentoxide under reduced pressure. The crude product was recrystallized from methanol and further purified by column chromatography (benzene/hexane 1:1) to give 16.2 g (56%) of **8** as white plates, mp 77-78°; ir (bromoform): 3440, 3400, 2920, 2850 cm^{-1}; ^1H nmr (DMSO-d_6): δ 11.36 (s, 1H, NH), 8.0-6.8 (m, 7H, aromatic protons), 2.97 (s, 4H, ring C_2H_4), 2.69 (t, 2H, J = 7.0 Hz, CH_2), 1.59-1.00 (m, 24H, $C_{12}H_{24}$), 0.84 (t, 3H, J = 4.0 Hz, CH_3); ^{13}C nmr (DMSO-d_6): 13.62, 21.61, 21.81, 28.49, 28.78, 31.07, 31.70, 35.46, 108.22, 110.90, 117.68, 121.14, 123.18, 124.35, 126.40, 127.62, 132.69, 133.32, 133.90, 134.68, 138.00.

Anal. Calcd. for $C_{30}H_{41}N$: C, 86.69; H, 9.94; N, 3.37. Found: C, 86.64; H, 9.96; N, 3.34.

10-Tetradecyl-7-*H*-benzo[*c*]carbazole **9**.

A mixture of dihydrobenzo[*c*]carbazole **8** (1.57 g, 3.8 mmoles) and 5% palladised carbon (0.23 g) was heated in a sand bath at 250-260° for 30 minutes. The reaction mixture was cooled and extracted with hot benzene (70 ml). The extracts were filtered and concentrated under reduced pressure. The brown residue was passed through a short column of silica gel to give a crude product which was recrystallized from methanol/hexane (1:1) to yield 1.11 g (71%) of **9** as white needles, mp 78-79°. An analytical sample was prepared by repeated crystallization from methanol/pentane; ir (bromoform): 3440, 3370, 2920, 2840, 1450, 800 cm^{-1}; ^1H nmr (DMSO-d_6): δ 11.80 (s, 1H, NH), 9.3-7.1 (m, 9H, aromatic protons), 2.83 (t, 2H, J = 7.0 Hz, CH_2), 2.6-0.9 (m, 24H, $C_{12}H_{24}$), 0.80 (t, 3H, J = 4.0 Hz, CH_3); ^{13}C nmr (DMSO-d_6): 13.77, 22.05, 29.07, 31.31, 32.14, 35.75, 111.14, 113.39, 113.78, 120.55, 122.16, 122.65, 123.09, 124.50, 126.40, 128.40, 128.93, 129.47, 133.27, 137.07, 137.61.

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