

NEW 6-(3-INDOLYL)BENZO[*b*]CARBAZOLES SENYAWA BARU 6-(3-INDOLYL)BENZO[*b*]KARBAZOL)

Mardi Santoso
Chemistry Department, Faculty of Science,
Sepuluh Nopember Institute of Technology Surabaya

ABSTRACT

Some attempts have been carried out to synthesize polycyclic heterocyclic compounds derived from new benzocarbazoles (**1**). New 6-(3-indolyl)benzo[*b*]-carbazoles (**2a**) have been synthesised in good yields from the reaction of simple indoles and *o*-phthalaldehyde in methanol catalysed by *p*-toulenesulfonic acid monohydrate. Their precise structure were established by microanalysis, spectroscopy, and X-ray crystallography of the benzo[*b*]carbazole (**2a**).

Keywords: indoles, polycyclic heterocyclic compounds, benzo[*b*]carbazoles

ABSTRAK

Beberapa usaha telah dilakukan untuk mensintesis senyawa-senyawa polisiklik heterosiklik dari senyawa-senyawa benzokarbazol baru (**1**). Empat 6-(3-indolil)benzo[*b*]karbazol baru (**2a**) telah disintesis dengan rendemen yang baik dari reaksi beberapa senyawa indol dengan *o*-phthalaldehyd dalam pelarut metanol yang dikatalisis oleh asam *p*-toulenasulfonat monohidrat. Struktur-struktur senyawa-senyawa baru ditetapkan dengan mikro- analisis, spektroskopi, dan kristalografi sinar-X dari benzo[*b*]karbazol (**2a**).

Kata kunci: senyawa indol, polisiklik heterosiklik, benzo[*b*]karbazol

INTRODUCTION

Since indoles are excessive heteroaromatic molecules, their chemistry are dominated by electrophilic substitutions such as protonation, nitration, nitrosation, sulfonation, halogenation, alkylation, acylation, and reaction with diazonium ions, azides, carbenes, carbonyl compounds, and immonium cations. However, the reactions of indoles with carbonyl compounds have attracted special attention. For instance, the simple acid catalysed reaction of indole with acetone has been studied for many years (Noland, *et al.*, 1996^a, Nolan *et al.*, 1996^b, Nolan and Venkiteswaran, 1961; Chaterjee, *et al.*, 1980; and Bergman *et al.*, 1989).

Interestingly, the reaction of 2,3-unsubstituted indoles with symmetrical dicarbonyl compounds has been only rarely explored (Ryang and Sakurai, 1972, Baneji *et al.*, 1993, and Baneji, 1994). The reaction of two equivalents of some simple indoles with one equivalent of *o*-phthalaldehyde in the presence of phosphoryl chloride has been investigated in previous work which gave new 11-(3-indolyl)benzo[*b*]carbazoles (**1**) in good yields. The structure of the benzocarbazoles were established by microanalysis, spectroscopy analysis and X-ray crystallography of the benzo[*b*]carbazole (**1a**) (Santosa, 2000). In view of the relative ease of constructing the indolylbenzo[*b*]carbazoles, some attempts have been carried out to form a link between the indolyl substituent and the main part of the carbazole ring which is reported in this paper.

EXPERIMENTAL METHOD

Equipments. Hitachi U-3200 Spectrophotometer, Perkin-Elmer Infrared spectrometer, Bruker AC300F spectrometer, AEI MS 12 mass spectrometer, Mel-Temp melting point apparatus, gravity column chromatography, "dry-column" flash column chromatography, short and long ultraviolet light.

Materials. 6-Bromonitrotoluene, 5-bromoindole, indole, *o*-phthalaldehyde, dimethyl formamide-dimethyl acetal, pyrrolidine, zinc, acetic acid, *p*-toluene sulfonic acid monohydrate, potassium hydroxide, dry

dimethyl sulfoxide, dry dimethyl formamide, anhydrous methanol, ether, water, dichloromethane, ethyl acetate, light petroleum (60-80 °C), magnesium sulfate, Merck 70-230 mesh silica gel, Merck 60H silica gel, iodine.

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| (a) R = H | R' = H |
| (b) R = CH ₃ | R' = H |
| (c) R = CH ₂ CH=CH ₂ | R' = H |

Figure 1. Structure 11-(3-indolyl)benzo[*b*]carbazole and its derivatives

Synthesis of 4-Bromoindole. 6-Bromonitrotoluene (1.55g, 7.64 mmol) in dry dimethyl formamide (30 mL) was treated with dimethyl formamide-dimethyl acetal (2.85mL, 21.45 mmol) and pyrrolidine (0.59mL, 7.07 mmol) with stirring, and the mixture was heated at 110 °C. After cooling, the mixture was diluted with ether and washed with water, and the aqueous phase was extracted with ether. The organic phase was dried over magnesium sulfate and evaporated under reduced pressure to yield the crude enamine. Then it was dissolved in 80 % aqueous acetic acid (40 mL) and heated to 75 °C, and zinc dust (4.06g, 62.10 mmol) was added portionwise for 90 minutes and the mixture heated at 85 °C for two hours. After cooling, the mixture was filtered and the filtrate was diluted with water, and extracted with dichloromethane. The combined extracts were washed with brine, dried over magnesium sulfate, evaporated under reduced pressure, and purified using "dry-column" flash chromatography (Harwood, 1985) with ethyl acetate/light petroleum (1/3) eluant to afford 4-bromoindole (0.68g, 49%) as a yellow oil (Moyer *et al.*, 1986). ¹H NMR (CDCl₃): 6.65, t, 1H, H3; 7.08, t, 1H, ArH; 7.23, t, 1H, H2; 7.32-7.35, m, 2H, ArH; 8.24, 1H, bs, NH. ¹³C NMR (CDCl₃): 102.92, 110.26, 122.70, 122.88, 124.75, ArCH; 114.66, 128.61, 135.97, ArC.

Synthesis of 6-(4-Bromoindol-3-yl)-1-bromobenzo[*b*]carbazole (2a), C₂₄H₁₄N₂Br₂. 4-Bromoindole (0.68g, 3.47 mmol) and *o*-phthalaldehyde (0.23g, 1.71 mmol) in anhydrous methanol (50 mL) were treated with *p*-toluene sulfonic acid monohydrate (0.35g, 1.84 mmol) and stirred for six days. The solution was concentrated and the residue diluted with water. The yellow precipitate was filtered off, washed with water, dried, and purified using "dry-column" flash chromatography with dichloromethane/light petroleum (2/1) eluant to yield the *carbazole* (2a) as a yellow solid (0.65g, 77%), Mp. 285-286 °C (Found C, 58.4; H, 2.6; N, 5.7, requires C, 58.8; H, 2.9; N, 5.7%). IR ν_{max} (Nujol) 3400, 1600, 1455, 1390, 1370, 1305, 1270, 1205, 1185, 1140, 905, 770, 755, 735 cm⁻¹, UV; λ_{max} (MeOH) 225 (ϵ 91,500), 278sh (ϵ 95,900), 284 (ϵ 98,000), 294sh (ϵ 53,400), 318 (ϵ 17,400), 333 (ϵ 15,300), 384 (ϵ 10,700), 404 nm (ϵ 13,100). ¹H NMR (CDCl₃): δ 7.13-9.32, m, 14H, ArH and NH. ¹³C NMR [(CD₃)₂SO]: δ 110.22, 111.74, 120.02, 122.23, 122.36, 122.62, 123.21, 125.14, 125.17, 127.83, 128.11, 129.01, ArCH; 109.33, 112.10, 113.33, 116.50, 120.80, 123.44, 126.25, 127.44, 133.70, 137.94, 140.42, 144.21, ArC. MS (EI): *m/e* 493 (M+1, ⁸¹Br, ⁸¹Br, 5%), 492 (M, ⁸¹Br, ⁸¹Br, 20), 491 (M+1, ⁸¹Br, ⁷⁹Br, 15), 490 (M, ⁸¹Br, ⁷⁹Br, 35), 489 (M+1, ⁷⁹Br, ⁷⁹Br, 10), 488 (M, ⁸¹Br, ⁷⁹Br, 20), 487 (2), 412 (15), 411 (20), 410 (30), 409 (20), 407 (5), 332 (20), 331 (25), 330 (70), 329 (45), 165 (100), 164 (50).

Crystals for a single crystal X-ray determination were obtained by recrystallization from dichloromethane/light petroleum.

Synthesis of 6-(5-Bromoindol-3-yl)-2-bromobenzo[*b*]carbazole (2b), C₂₄H₁₄N₂Br₂.1/2H₂O. 5-Bromoindole (0.52g, 2.65 mmol) and *o*-phthalaldehyde (0.18g, 1.34 mmol) were treated with *p*-toluene sulfonic acid monohydrate (0.27g, 1.42 mmol) in anhydrous methanol (35 mL) and stirred for 52 hours at room temperature. The solution was concentrated under reduced pressure and water was added. The resulting yellow

precipitate was filtered off, washed with water, dried, and purified using gravity column chromatography with dichloromethane/light petroleum (2/1) eluant to afford the *carbazole* (**2b**) $C_{24}H_{14}N_2Br_2 \cdot 1/2H_2O$ as a bright yellow solid (0.51g, 78%), MP. 273-274 °C (Found C, 57.7; H, 2.7; N, 5.5%, requires C, 57.7; H, 3.0; N, 5.6%). IR; V_{max} . (Nujol) 3440, 3410, 1630, 1450, 1410, 1375, 1270, 1230, 1190, 1150, 840, 800, 790, 750, 740, 670 cm^{-1} . UV λ_{max} . (MeOH) 223 (ϵ 111,100), 271 (ϵ 106,200), 282sh (ϵ 85,000), 301 (ϵ 60,500), 320 (ϵ 26,200), 334 (ϵ 16,300), 392sh (ϵ 11,900), 408 nm (ϵ 12,600). 1H NMR ($CDCl_3$): δ 7.16-8.59, 14H, ArH and NH. ^{13}C NMR [$(CD_3)_2SO$]: δ 113.03, 114.16, 118.81, 121.32, 122.59, 123.71, 124.08, 124.87, 125.23, 127.80, 129.00 and 129.65, ArCH; 108.95, 110.55, 110.81, 111.91, 123.73, 124.70, 128.17, 129.46, 131.67, 135.45, 139.46 and 141.48, ArC. MS (EI): m/e 493 (M+1, ^{81}Br , ^{81}Br , 10%), 492 (M, ^{81}Br , ^{81}Br , 25), 491 (M+1, ^{81}Br , ^{79}Br , 15), 490 (M, ^{81}Br , ^{79}Br , 50), 489 (M+1, ^{79}Br , ^{79}Br , 10), 488 (M, ^{81}Br , ^{79}Br , 25), 410 (10), 165 (100).

Synthesis of 6-(Indol-3-yl)benzo[b]carbazole (2c) $C_{24}H_{16}N_2 \cdot 1/4H_2O$. Indole (1.37g, 11.69 mmol) and *o*-phthalaldehyde (0.78g, 5.82 mmol) in anhydrous methanol (50 mL) were treated with *p*-toluene sulfonic acid monohydrate (1.21g, 6.36 mmol), and the solution was stirred for four hours. The mixture was concentrated and the residue diluted with water. The crude product was filtered off, washed with water, dried, and purified using "dry-column" flash chromatography with dichloromethane/light petroleum (1/1) eluent to yield the *carbazole* (**2c**) as a bright yellow solid (1.53g, 79%), m. p. 130-131 °C (dec.) (Found C, 85.8; H, 4.7; N, 8.4% $C_{24}H_{16}N_2 \cdot 1/4H_2O$ requires C, 85.6; H, 4.9; N, 8.3%). IR; V_{max} . (Nujol) 3400, 1605, 1440, 1370, 1320, 1220, 1150, 730 cm^{-1} . UV, λ_{max} . (MeOH) 223 (ϵ 105,000), 272 (ϵ 122,300), 281sh (ϵ 105,000), 293sh (ϵ 61,200), 320 (ϵ 17,300), 334 (ϵ 16,000), 382sh (ϵ 12,900), 400 nm (ϵ 14,600). 1H NMR ($CDCl_3$): δ 7.13-8.67, 16H, m, ArH and NH. ^{13}C NMR ($CDCl_3$): δ 110.25, 111.52, 118.09, 119.31, 120.29, 120.36, 121.14, 122.59, 122.68, 124.43, 124.94, 125.11, 127.23, 128.81, ArCH; 110.65, 111.29, 123.46, 127.34, 131.81, 136.31, 138.88, 141.72 ArC. MS (EI): m/e 333 (M+1, 25%), 332 (M, 100), 331 (50); 330 (30), 165 (10).

Synthesis of 6-(4-Bromo-1-methylindol-3-yl)-1-bromo-5-methylbenzo[b]-carbazole (3) $C_{26}H_{18}N_2Br_2$. 6-(4-Bromoindol-3-yl)-1-bromo-benzo[b]carbazole (**2a**) (0.18g, 0.37 mmol) and freshly crushed potassium hydroxide (0.16g, 2.85 mmol) in dry dimethyl sulfoxide (20 mL) were stirred for two hours at room temperature. Iodomethane (0.09 mL, 1.45 mmol) was added and the mixture was stirred for an additional two hours. Water was added and the resulting precipitate was filtered off, washed with water, dried and purified using "dry-column" flash chromatography with dichloromethane/ light petroleum (1/1) to afford the *carbazole* (**3**) as a bright yellow solid (0.18g, 95%), m. p. 237-238 °C (Found C, 60.8; H, 3.4; N, 5.4%; $C_{26}H_{18}N_2Br_2$ requires C, 60.3; H, 3.5; N, 5.4%). IR; V_{max} . 1590, 1455, 1410, 1390, 1320, 1280, 1260, 1190, 1170, 1120, 1060, 1015, 960, 875, 860, 840, 800, 760, 735, 720 cm^{-1} . UV; λ_{max} . (MeOH) 229 (ϵ 64,100), 288 (ϵ 73,900), 297 (ϵ 44,700), 319 (ϵ 12,300), 334 (ϵ 6,500), 387 (ϵ 5,900), 409 nm (ϵ 7,800). 1H NMR ($CDCl_3$): δ 3.33 and 3.92, 2s, 6H, CH_3 ; 7.12-7.46, m, 9H, ArH; 7.59, d, $J=8.3Hz$, 1H, ArH; 8.14, d, $J=8.3Hz$, 1H, ArH; 9.44, s, 1H, ArH. ^{13}C NMR ($CDCl_3$): δ 31.75 and 33.37, CH_3 ; 106.99, 108.86, 121.63, 122.59, 123.06, 123.18, 124.14, 125.32, 125.46, 127.30, 128.93, 131.00, ArCH; 110.74, 111.51, 115.34, 117.46, 121.11, 124.60, 127.62, 128.31, 135.04, 137.72, 140.30, 145.79, ArC. MS; (EI): m/e 521 (M+1, ^{81}Br , ^{81}Br , 10%), 520 (M, ^{81}Br , ^{81}Br , 35), 519 (M+1, ^{81}Br , ^{79}Br , 15), 518 (M, ^{81}Br , ^{81}Br , 65), 517 (M+1, ^{79}Br , ^{79}Br , 10), 516 (M, ^{79}Br , ^{79}Br , 35), 438 (10), 424 (45), 422 (45), 409 (15), 407 (15), 178 (100).

RESULTS AND DISCUSSION

Some attempts have been explored to synthesize new polycyclic heterocyclic compounds derived from new benzocarbazoles (**1**). The first conditions used oxalyl chloride which was designed to form a new seven or eight membered ring, after initial reaction at the C2 position. However the benzo[*b*]carbazoles (**1**) failed to yield any product after stirring at room temperature for three days. Akermark *et al.*, 1975) reported the intramolecular cyclization of diphenylamine (**4**) to carbazole (**5**) in 70% when it was heated in acetic acid containing palladium acetate (figure 2 a). Miller and Mock (1980), also reported the use of palladium acetate in the intramolecular cyclization of anilinoisoquinoline (**6**) in the last step of the synthesis of ellipticine (**7**) (figure 2b). Following these methods, intramolecular cyclization of the indolyl carbazole was attempted. However, the indolyl benzocarbazole (**1a**) did not react when treated for five days with palladium acetate in acetic acid, but decomposed when treated according the Miller and Mock method.

(a). Cyclization reaction of diphenylamine (**4**) to carbazol (**5**)

(b). Cyclization reaction anilinoisoquinoline (**6**) to ellipticine (**7**)
Figure 2. Two types of cyclization reaction of hetero cyclic compounds

Although aryl-aryl coupling requires stoichiometric quantities of palladium acetate, the process is known to be catalytic for halo-aryl compounds. Several examples are the synthesis of carbazole-1-carboxylic acid (**9**) from *N*-(2-iodophenyl) anthranilic acid (**8**) Sakamoto, *et al.*, 1988 (figure 3 a), and the synthesis of the tetracycle (**11**) from *N*-(*o*-bromobenzyl)indole (**10**) Kozikowski and Ma 1991 (figure 3 b). Investigation of the intramolecular aryl-aryl coupling of the indolyl benzocarbazoles was continued by preparing similar benzocarbazoles bearing halogen atoms. The reaction of 4- and 5-bromoindole with *o*-phthaldialdehyde was carried out in order to yield the benzocarbazoles (**12**), (figure 4), but the presence of bromine atoms caused the reaction to give more complex products. Therefore, the reaction was performed using a different catalyst, namely *p*-toulenesulfonic acid monohydrate (ptsa). In contrast to the previous conditions, the reaction of 4-bromoindole and the dialdehyde catalysed by ptsa was very slow requiring six days at room temperature, but purification of the crude product was easier and the product yield was higher (77%). The ¹H NMR of the product was inconclusive. However, single crystal X-ray crystallography clearly established in Figure 5, that the product was a benzo [*b*]carbazole with the 6-position substituted by indole, namely 6-(4- bromoindol-3-yl)-1-bromobenzo [*b*]carbazole (**2a**). Consequently, the two catalysts gave different condensation products. 5-Bromoindole and indole were also reacted with the dialdehyde in the presence of ptsa and afforded the condensation products (**2b-c**) in good yields, showing the generality of this reaction.

(a). Cyclization reaction of anthranilic acid (8) to carbazo-1-carboxylic acid (9)

(b). Cyclization of *N*-(*o*-bromobenzyl)indol (10) to tetracycle

Figure 3. Two methods of cyclization reaction of indol (a) anthranilic acid and (b) *o*-brom benzyl indol

(a) R = H R' = Br
(b) R = Br R' = H

(a) R = H R' = Br
(b) R = Br R' = H
(c) R = H R' =

Figure 4. Indol derivatives, (12) benzocarbols and 6-(4-bromoindol-3-yl)-1-bromobenzol[*b*] carbazoles (2)

Figure5: X-ray crystal structure of the benzo[*b*]carbazole (**2a**)

As a result, the electrophilic substitution of simple indoles and *o*-phthaldialdehyde catalysed by ptsa instead of phosphoryl chloride afforded the isomeric, 6-substituted benzo[*b*]carbazoles which can be considered as 2-deaza-ellipticine derivatives, and according to Pindur and collaborators Pindur *et al.*, 1992, and Drager *et al.*, 1993 these could exhibit potential as DNA intercalators. Consequently, the condensation of simple indoles and the dialdehyde catalysed by ptsa requires a different reaction mechanism, possibly that outlined in figure 6.

Figure 6. Cyclization reaction of indol derivative (benzocarbazole) using *p*-toluenesulfonic acid (ptsa).

This requires an attack of one indole on each aldehyde, as opposed to the attack of two indoles on one aldehyde. Cyclization at the indole C2 then forms a six-membered ring and dehydration then generates the aromatic product. Presumably, the use of a weaker catalyst, leading to a much slower reaction, favours the formation of the intermediate arising from attack of one indole at each aldehyde.

Methylation of the benzocarbazole (**2a**) has been carried out following Heaney and Ley's method 1973, and 1974, which gave the *N*-methylated benzocarbazole (**12**) in 95% yield. Palladium catalysed intramolecular cyclization of the benzocarbazole (**12**) was attempted following the cyclization method for *N*-(*o*-bromobenzyl)indole Kozikowski and Ma, 1991, as mentioned above, in order to give the heteropolycyclic compound (**13**). However, no reaction occurred even after 41 hours. It appears that the failure to effect cyclization of either the 6- or 11-indolyl benzocarbazoles is probably the result of steric problems in the transition states.

(12)

Figure 7. N-Methylated heterocyclic compounds

CONCLUSION

Reaction of simple indoles and *o*-phthaldialdehyde in anhydrous methanol catalysed by pTSA afforded new 6-(3-Indolyl)benzo[*b*]carbazoles (**2**) in good yields, and methylation of the carbazoles (**2a**) gave new carbazole (**3**) in quantitative yield. The failure to build polycyclic heterocyclic compounds derived from new benzocarbazoles (**1**) and (**3**) is probably the result of steric problems in the transition states.

ACKNOWLEDGEMENT

The author is grateful to Professor David StC. Black of School of Chemistry, Faculty of Science and Technology, The University of New South Wales, for generous assistance and discussion. The author wishes to thank to Don Craig of UNSW for crystallography; Dr. Joe Brophy of UNSW for the measurement of mass spectra; and last but not the least to Reet Bergman of Microanalytical Unit, Research School of Chemistry, The Australian National University for microanalysis.

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Indolyl)benzo(b)carbazole

New-6-(3-

Saantoso

Indolyl)benzo(b)carbazole

New-6-(3-

Saantoso