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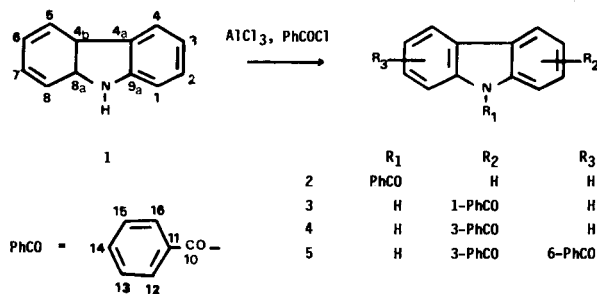
By heating carbazole (**1**) with aluminum trichloride and benzoyl chloride four benzoylcarbazole derivatives were obtained: *N*-benzoylcarbazole (**2**), 1-benzoylcarbazole (**3**), 3-benzoylcarbazole (**4**) and 3,6-dibenzoylcarbazole (**5**). The complete characterization of benzoylcarbazole derivatives **2-5** was performed by physical and spectroscopical methods (mp, tlc R_f , glc T_r , uv, ir, ^1H nmr, ^{13}C nmr and ms).

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As part of an ongoing program that is involved with the photochemical behavior of nitrogen organic compounds (amines [1-4] and alkaloids [5-8]), we have examined the photochemical reaction of carbazole [1,2], azacarbazole [5,7] and *N*-acetylcarbazole [9]. Lately we have been studying the photochemical reactions of *N*-benzoylcarbazole and we decided to prepare as an authentic sample, 3,6-dibenzoylcarbazole. According to our knowledge the synthesis of this compound was described by Plant *et al.* a long time ago [10] and since this data only its melting point and analysis have been described.

We now report a convenient reinvestigation of the method described by Plant [10] for the thermal synthesis of 3,6-dibenzoylcarbazole in which 3,6-dibenzoylcarbazole (**5**) together with *N*-benzoyl **2**, 1-benzoyl **3** and 3-benzoylcarbazole (**4**) were obtained (Scheme 1).

Scheme 1



It is interesting to note that as result of our studies we could also prepare 1-benzoylcarbazole (**3**) whose synthesis had not been previously described in the literature and we could also obtain the spectroscopic data (uv, ir, ^1H nmr, ^{13}C nmr, and ms) for *N*-benzoyl **2** and 3-benzoylcarbazole (**4**) which have not been described yet.

After the action of benzoyl chloride on carbazole in carbon disulphide solution in the presence of aluminum chloride, 3,6-dibenzoylcarbazole was described as the only reaction product by Plant *et al.* [10]. This compound obtained as pale yellow plates was characterized by its mp (258°) and by analysis [10]. Its constitution was established by its formation from 5:4'-dibenzoyl-1-phenylbenzotriazole, prepared by condensing 4-bromo-3-nitrobenzophe-

none and *p*-aminobenzophenone, followed by reduction and treatment with nitrous acid [10]. Plant *et al.* also say that all efforts to synthesize 1-benzoylcarbazole were unsuccessful [10].

In our hands the thermal treatment of carbazole (**1**) with aluminum trichloride and benzoyl chloride in carbon disulphide solution according to the Plant method [10] produced a complex mixture (tlc) as a pasty blue-green solid. The main components of the mixture were isolated by column chromatography and identified by spectroscopic methods as benzoylcarbazole derivatives: *N*-benzoyl **2**, 1-benzoyl **3**, 3-benzoyl **4** and 3,6-dibenzoylcarbazole (**5**). An unidentified mixture of oily polymeric compounds were also obtained.

In order to increase the formation of compound **5** we repeated the attempt at different carbazole:aluminum trichloride:benzoyl chloride molar ratio and refluxing the mixture during different times. When the reaction was conducted under nitrogen atmosphere (46°, 1 hour) a blue solid was isolated from which compounds **3**, **4** and **5** were obtained in the highest yield and no polymeric products were isolated (see Experimental).

It is interesting to note that in our hands this reaction never yielded 3,6-dibenzoylcarbazole as the only benzoylcarbazole derivative. The structures of compounds **2-5** were established taking into account elemental analyses and spectral data (see Experimental).

The assignments of the ^{13}C resonances were based on chemical shift correlations, signal intensities in the partially relaxed spectra and multiplicities in some off-resonance proton decoupled spectra. The assignments of the ^{13}C chemical shifts of quaternary carbons were confirmed using the SPDD method, a procedure for the determination of carbon multiplicities which is based on a delayed decoupling technique [11]. The ^{13}C nmr spectra were measured using 35° pulse and a pulse repetition rate of 0.75 s. All spectra were also measured using 45° pulses; this pulse width and the repetition rate of the pulses (0.75 s) were chosen since carbon nuclei with long relaxation times (those with no directly bonded protons) would either not be observed or have low intensities. The assignments of

the chemical shifts of 2-C and 4-C of compound **3**, 2-C and 4-C of compound **4** and 2-C, 4-C, 5-C and 7-C of compound **5** were confirmed using the off-resonance C-[H] spin decoupling graphical method of assigning ^{13}C absorptions by connecting the residual splitting (J_r) with the proton frequency signals from directly bonded protons of known assignment [12-15]. In all cases, comparisons were made with calculated chemical shifts obtained by semi-empirical rules using indole [15], carbazole [16], benzophenone and acetophenone [17] as model compounds and known substituent-induced shifts for monosubstituted benzenes [18]. The ^{13}C nmr data are compiled in the Experimental.

The ^1H nmr assignments have been made taking into account the chemical shifts and multiplicities. From the Dreiding Model of **3** it can be seen that the benzoyl group at 1-C has its carbonyl group close to 9-H (H-N, Figure 1). This spatial interaction can account for an intramolecular hydrogen bridge involving both groups which explains that the polarity of compound **3** is lower than that of compound **4**; a higher R_f value (tlc) and a lower T_r value (glc) for **3** are observed (*N*-benzoylcarbazole, R_f 0.79, T_r 16.6; 1-benzoyl carbazole, R_f 0.75, T_r 19.2; 3-benzoylcarbazole, R_f 0.21, T_r 29.7). Besides, by comparing the ^1H nmr spectrum of **3** with the calculated ^1H nmr data obtained by semi-empirical rules we can observe a deshielding effect on 2-H ($\Delta\delta$ 2-H = 0.42 ppm, δ 2-H calculated 7.75 ppm) which together with the NH signal at δ 6.90 ppm suggests a structure like that shown in Figure 1 for compound **3**. Finally, by comparing the ^1H nmr spectra of *N*-benzoyl carbazole (**2**) and *N*-acetylcarbazole (see Experimental) we can observe a shielding effect on 1-H and 8-H groups which suggests that the phenyl group of the *N*-benzoyl moiety and the carbazolyl group lie in almost perpendicular planes thus the unshared *N* electrons and the carbonyl group are *anti* to each other giving a stable conformation (*N*-acetylcarbazole, 1-H and 8-H 8.21 ppm, 4-H and 5-H 8.02 ppm; *N*-benzoylcarbazole, 1-H and 8-H 7.62 ppm, 4-H and 5-H 8.00 ppm). The shielding effect observed on 12-H and 16-H, both *ortho* to the carbonyl group in the benzoyl moiety (δ 7.70 ppm), agrees with the proposed conformation (Figure 2).

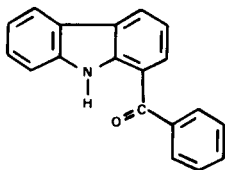


Figure 1

Also, the microanalyses data and the mass spectra data support the structures assigned to the products **2-5**. The major cleavage of these compounds upon electron impact may be plausibly interpreted as follows: As it is shown in

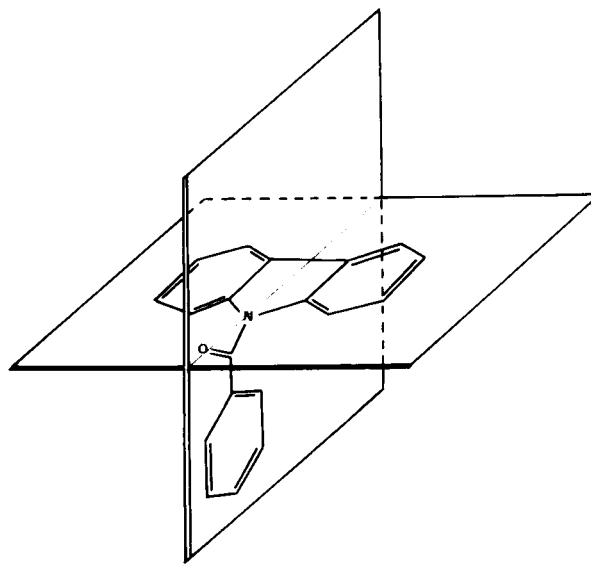
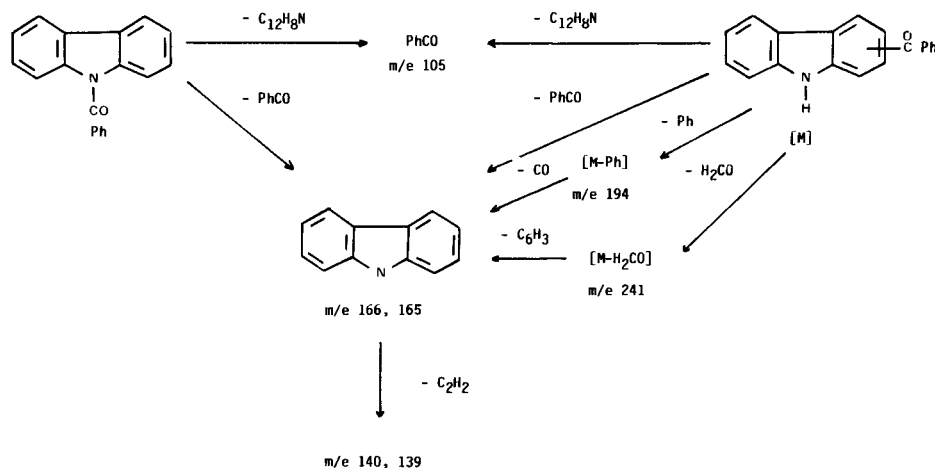


Figure 2

the Experimental, the molecular ion peak is a very important peak, sometimes the base peak in the mass spectra of the benzoyl carbazoles **3-5**. All compounds are very stable under electron impact due to their heteroaromaticity which favors the molecular ion to be observed as a very important peak [19-22]. An interesting relationship between the position of the benzoyl substituent in the carbazole ring and the fragmentation patterns has been observed. Loss of the H_2CO and Ph group from the molecular ion ($\text{M}-\text{H}_2\text{CO}$, m/e 241 and $\text{M}-\text{Ph}$, m/e 194) are observed in the mass spectra of 1-benzoylcarbazole (**3**) and 3-benzoylcarbazole (**4**) together with the loss of the PhCO group ($\text{M}-\text{PhCO}$, m/e 166) (Scheme 2). The lack of both ions ($\text{M}-\text{H}_2\text{CO}$ and $\text{M}-\text{Ph}$) in the mass spectrum of *N*-benzoylcarbazole (**2**) and the presence of the $\text{M}-\text{PhCO}$ fragment (m/e 166) can be explained taking into account that both, the former mentioned fragments are typical of benzophenone-type compounds [21]. The fragmentation paths of **2**, involving expulsion of PhCO fragment and of **3** and **4** involving H_2CO , Ph and PhCO fragments have been demonstrated by the presence of metastable ions. The mass spectra of benzoylcarbazoles **2-5** are compiled in the Experimental and as is known [21-23] the fragmentation behavior of aromatic amides and benzophenones are relatively simple.

The introduction of PhCO substituents into both the 3- and the 6-position of carbazole (3,6-dibenzoylcarbazole, **5**) results in a fragmentation pathway similar to that observed for **3** and **4**. In addition we compared these spectra, **2-5**, with that of carbazole (see ref [2]) and a good correlation was observed (ions of m/e 166, 165, 141, 140, 139, 77, 57, and 43).

Scheme 2



As expected the peaks of m/e 106 and 105 are pronounced peaks in all spectra of benzoylcarbazoles **2-5**, being a good evidence of the formation of a common ion, the benzoylinium ions (PhCHO and PhCO).

In conclusion, compounds **2-5** give characteristic fragments with high intensities under electron impact and characteristic ^1H nmr and ^{13}C nmr signals which agree with the elemental analytical data and the structures assigned shown in Scheme 1.

EXPERIMENTAL

The uv absorption spectra were recorded using a Hewlett Packard HP 8451 A - uv/visible diode array spectrophotometer; shoulder positions were identified with the first and second derivatives of the absorbance data. All the measurements were made with 1 cm stoppered quartz cells at 25-28°. The ir spectra were recorded on neat samples, using the Nujol technique for solids, with a Perkin-Elmer M 710 B spectrophotometer. The hplc analyses were conducted on a Micromeritics chromatograph using an Altech Ultrasphere ODS-2 5 μm (250 x 10 mm) using methanol-water mixtures as eluent. Mass spectra were recorded on a Varian-MAT CH 7-A spectrometer interfaced to a Varian-MAT data system 166 computer, at 70 eV (direct inlet). Preliminary glc analysis was performed with a Hewlett Packard research gas chromatograph 5840 A/18850 A equipped with a capillary column (SP-2100, 12 m x 0.25 mm x 0.2 μm film; carrier: Helium, 10 ml/min; oven: temperature program 100-400°, rate 8°/min; detector: FID). The same apparatus was employed for quantitative analysis using internal standards. The glc-ms data were obtained with a glc-Varian Aerograph 1400/ms-Varian MAT CH-7A/Data System 166. The most intense peaks (abundance relative \geq 3%) are reported in this work. Melting points are uncorrected and were determined on a Kofler hot-plate apparatus. The ^1H and ^{13}C -FT nmr spectra were recorded on a Varian XL-100-15 spectrometer at 100 and 25 MHz respectively in deuteriochloroform-TMS solutions. Totally proton decoupled spectra are the results of 10000 pulses, and were obtained by irradiation of the ^1H spectrum at the central frequency of 5 ppm, with the irradiation frequency modulated by an external swept square-wave modulator.

Single-frequency off-resonance ^1H decoupled spectra are the result of 25000 pulses, and were obtained by irradiating the ^1H spectrum with a CW frequency at *ca* 0 ppm. Proton off-resonance decoupled carbazoles ^{13}C spectra were obtained as above, by irradiating the ^1H spectrum with a CW frequency at *ca* 10 ppm downfield from TMS. Selectively decoupled spectra were obtained as above, but irradiating the desired ^1H resonance with a low-power CW frequency. Lines were artificially broadened by *ca* 1 Hz by exponential weighting of the FID.

General Procedure for the Reaction of Carbazole with Benzoyl Chloride.

All of these reactions were carried out under a nitrogen atmosphere. To a solution of carbazole (**1**, Hopkin & Williams LTD) (1.09 g, 6.55 mmoles) and aluminum trichloride (Merck) (0.91 g, 6.90 mmoles) in dry carbon disulphure (Mallinckrodt SpectrAR) (10 ml, bp 46.5°) was added drop by drop benzoyl chloride (Merck) (0.91 g, 6.51 mmoles) stirring the mixture at room temperature with the aid of a magnetic stirrer. After being refluxed for 1 hour the red solution was evaporated *in vacuo* to dryness. The residual semisolid was treated with an acidic aqueous solution (10 ml water and 0.12 ml of hydrochloric acid) and extracted with methylene chloride. The organic phase was washed with bicarbonate aqueous solution, with water and dried over magnesium sulphate. Evaporation of methylene chloride *in vacuo* gave a residue, which was recrystallized from methanol to give a complex mixture (tlc). The main components of the mixture were isolated by silica-gel (Merck, Kieselgel 60) column chromatography, prepacked in hexane. Elution of the column with hexane-ethyl acetate mixtures gave unconverted carbazole and compounds **2**, **3**, **4** and **5** as follows:

The unconverted carbazole was obtained as colorless prisms (ethanol) (7 mg, conversion 93%) from the first eluted fraction and was characterized by its physical and spectroscopical properties (mp, tlc R_f 0.82, glc T_r 8.4 [1,2]).

N-Benzoylcarbazole (**2**).

This compound was obtained as colorless needles (ethanol) mp 97-98° [24] from the second eluted fraction (1 mg, 1.1% yield); tlc R_f 0.79; glc T_r 16.6; ir (Nujol): 1670 (CO), 1590, 1510 cm^{-1} (aromatic); uv (ethanol): λ max 280 (log ϵ 4.35), 310 (log ϵ 4.02), 370

nm (log ϵ 2.22); ^1H nmr (deuteriochloroform): δ 7.20-7.50 (m, 7 H, 2-, 3-, 6-, 7-, 13-, 14-, and 15-H), 7.62 (dd, 2 H, 1- and 8-H, $J = 1.5$, 7.0 Hz), 7.70 (dd, 2H, 12- and 16-H, $J = 2.0$, 8.0 Hz), 8.00 ppm (dd, 2 H, 4- and 5-H, $J = 1.5$, 6.0 Hz); ^{13}C nmr (deuteriochloroform): δ 115.7 (1-C), 119.7 (3-C), 123.2 (4-C), 125.9 (4_a-C), 126.6 (2-C), 128.7 (12-C), 128.9 (13-C), 132.2 (14-C), 135.6 (11-C), 139.2 (9_a-C), 169.4 ppm (CO); ms: (m/e) 272 (7), 271 (M⁺, 34), 166 (7), 140 (5), 106 (12), 105 (100), 78 (5), 77 (80), 57 (10), 43 (5).

Anal. Calcd. for C₁₉H₁₃NO: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.07; H, 4.81; N, 5.14.

1-Benzoylcarbazole (3).

This compound was obtained as yellow needles (ethanol) mp 123-125°, from the third eluted fraction (7 mg, 7.5% yield); tlc R_f 0.75; glc T, 19.2; ir (Nujol): 3525 (broad, NH), 1666 (CO), 1592, 1460 cm⁻¹ (aromatic); uv (ethanol): λ max 280 (log ϵ 4.38), 312 (log ϵ 4.05), 374 nm (log ϵ 2.42); ^1H nmr (deuteriochloroform): δ 6.90 (broad s, 1 H, NH, deuterium oxide-exchangeable), 7.18-7.38 (m, 3 H, 6-, 7- and 8-H), 7.52 (m, 4 H, 3-, 13-, 14- and 15-H), 7.83 (dd, 2 H, 12- and 16-H, $J = 2.0$, 8.0 Hz), 8.11 (dd, 1 H, 5-H, $J = 1.5$, 6.0 Hz), 8.17 (dd, 1 H, 2-H, $J = 2.0$, 8.0 Hz), 8.36 ppm (dd, 1 H, 4-H, $J = 1.5$, 7.0 Hz); ^{13}C nmr (deuteriochloroform): δ 110.3 (8-C), 117.8 (5-C), 118.3 (6-C), 119.3 (3-C), 120.1 (1-C), 122.1 (4_a-C), 124.8 (4_b-C), 125.6 (2-C), 125.8 (7-C), 126.5 (4-C), 128.1 (13- and 15-C), 129.2 (12- and 16-C), 130.6 (11-C), 131.3 (14-C), 138.2 (9_a-C), 143 (8_c-C), 197.4 ppm (CO); ms: (m/e) 272 (15), 271 (M⁺, 100), 270 (9), 242 (4), 241 (13), 195 (5), 194 (18), 193 (5), 167 (4), 166 (30), 140 (3), 139 (6), 105 (9), 77 (4), 57 (5), 43 (3).

Anal. Calcd. for C₁₉H₁₃NO: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.09; H, 4.90; N, 5.12.

3-Benzoylcarbazole (4).

This compound was obtained as pale yellow plates (ethanol) mp 213-215° (lit 203-205° [10-24]), from the fourth eluted fraction (20 mg, 22% yield); tlc R_f 0.21; glc T, 29.7; ir (Nujol): 3527 (broad, NH), 1667 (CO), 1590, 1450 cm⁻¹ (aromatic); uv (ethanol): λ max 216 (log ϵ 4.70), 235 (log ϵ 4.60), 280 (log ϵ 4.58), 291 (log ϵ 4.56), 329 nm (log ϵ 4.26); ^1H nmr (deuteriochloroform): δ 7.20-7.40 (m, 3 H, 6-, 7- and 8-H), 7.54 (m, 4 H, 1-, 13-, 14- and 15-H), 7.86 (dd, 2 H, 12- and 16-H, $J = 2.0$, 8.0 Hz), 7.92 (dd, 1 H, 5-H, $J = 1.5$, 6.0 Hz), 8.10 (dd, 1 H, 2-H, $J = 2.0$, 8.0 Hz), 8.49 (broad s, 1 H, NH, deuterium oxide-exchangeable), 8.59 ppm (d, 1 H, 4-H, $J = 1.5$ Hz); ^{13}C nmr (deuteriochloroform): δ 111.0 (8-C), 111.8 (1-C), 120.3 (5-C), 120.9 (4-C), 123.3 (4_a-C), 123.7 (4_b-C), 124.6 (7-C), 126.9 (2-C), 128.5 (3-C), 128.6 (11-C), 128.7 (13- and 15-C), 130.3 (12- and 16-C), 132.4 (14-C), 139.4 (8_a-C), 141.2 (9_a-C), 198.4 ppm (CO); ms: (m/e) 272 (28), 271 (M⁺, 100), 270 (11), 242 (8), 241 (17), 195 (20), 194 (100), 167 (7), 166 (37), 165 (5), 140 (5), 139 (19), 105 (7), 77 (9), 57 (7), 43 (5).

Anal. Calcd. for C₁₉H₁₃NO: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.12; H, 4.77; N, 5.18.

3,6-Dibenzoylcarbazole (5).

This compound was obtained as pale yellow needles (ethanol) mp 262-263° (lit 243° [10]), from the fifth eluted fraction (65 mg, 70% yield); tlc R_f 0.10; glc T, 58; ir (Nujol): 3525 (broad, NH), 1665 (CO), 1590, 1470 cm⁻¹ (aromatic); uv (ethanol): λ max 216 (log ϵ 4.75), 230 (log ϵ 4.78), 269 (log ϵ 4.81), 300 (log ϵ 4.73), 341 nm (log ϵ 4.60); ^1H nmr (deuteriochloroform): δ 7.58 (m, 8 H, 1-, 8-, 13-, 14-, 15-, 13', 14' and 15'-H), 7.86 (dd, 4 H, 12-, 16-, 12' and 16'-H, $J = 2.0$, 8.0 Hz), 8.05 (dd, 2 H, 2- and 7-H, $J = 2.0$, 8.0 Hz), 8.58 (d, 2 H, 4- and 5-H, $J = 2$ Hz), 8.83 ppm (broad

s, 1 H, NH, deuterium oxide-exchangeable); ^{13}C nmr (deuteriochloroform): δ 110.6 (1- and 8-C), 122.8 (4_a- and 4_b-C), 123.9 (4- and 5-C), 127.9 (2- and 7-C), 128.1 (13-, 15-, 13' and 15'-C), 129.0 (11- and 11'-C), 129.7 (12-, 16-, 12' and 16'-C), 130.0 (3- and 6-C), 131.8 (14- and 14'-C), 138.3 ppm (8_a- and 9_a-C); ms: (m/e) 376 (11), 375 (M⁺, 74), 345 (9), 299 (7), 298 (23), 272 (16), 271 (63), 270 (11), 243 (11), 241 (15), 237 (8), 197 (14), 195 (12), 194 (48), 193 (13), 168 (14), 167 (28), 166 (23), 165 (14), 141 (30), 140 (16), 139 (28), 105 (100), 77 (40), 57 (10), 43 (65).

Anal. Calcd. for C₂₃H₁₇NO₂: C, 82.03; H, 4.88; N, 3.99. Found: C, 82.09; H, 4.83; N, 3.97.

N-Acetylcarbazole.

This compound has been prepared by the method described by us [9]. The melting point, elemental analysis, uv, ^{13}C nmr and mass spectrum have been previously reported [9]; ^1H nmr (deuteriochloroform): δ 2.88 (s, 3 H, CH₃), 7.34-7.52 (m, 4 H, 2-, 3-, 6- and 7-H), 8.02 (dd, 2 H, 4- and 5-H, $J = 2.0$, 8.0 Hz), 8.21 (dd, 2 H, 1- and 8-H, $J = 2.0$, 8.5 Hz).

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