Synthesis and conformation of 5,6,7,8-tetrahydrodibenz[*c*,*e*]azocine

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Received 1 October 1990

A simplified four- or alternatively five-step synthesis of 5,6,7,8-tetrahydrodibenz[*c*,*e*]azocine from phenanthrene is described. The latter was ozonolyzed to the known 3,8-dimethoxydibenzo[*c*,*e*][1,2]dioxacyclooctane, which, when treated with alkylamine and nitromethane afforded methyl 2-(2-nitroethenyl)-2′-biphenylcarboxylate. Its hydrogenation followed by cyclization at elevated temperature yielded 2-(2-aminoethyl) derivative *V* and 5,6,7,8-tetrahydrodibenz[*c*,*e*]azocin-5-one, respectively. Reduction of the lactam ring of the substituted azocinone furnished the final product, which can alternatively be obtained directly from compound *V* on reaction with sodium bis(2-methoxyethoxy)hydridoaluminate. Conformation of the final product was deduced from ^{1}H and ^{13}C NMR and UV spectral data.

Pharmacologically effective derivatives of apogalanthamine prompted us to search for a suitable method for preparation of the structurally related 5,6,7,8-tetrahydrodibenz[*c*,*e*]azocine (*VII*). As found, various methods could be applied; thus, 6,7-dihydro-5*H*-dibenzo[*a*,*c*]cycloheptan-6-one, obtained from phenanthrene by a six-step synthesis, could be reacted in two ways: Beckmann rearrangement of the corresponding oxime furnished 5,6,7,8-tetrahydrodibenz[*c*,*e*]azocin-7-one and its reduction with lithium hydridoaluminate gave the compound *VII* [1]. The second variation employed the Schmidt reaction with azoimide in phosphoric and trichloroacetic acids [2] instead of the Beckmann rearrangement. Another procedure [3] starting from phenanthrene involved 7 steps; from phenanthrene *via* α,2′-(2-methylbiphenyl)carbolactone, methyl 2-(bromomethyl)-2′-biphenylcarboxylate, 2-(cyanomethyl) derivative, its reduction to 2-(2-aminoethyl)-2′-(hydroxymethyl)biphenyl and reaction with phosphorus tribromide to the required product *VII*. A long-term photolysis of *N*-(2-iodobenzyl)-*N*-(2-phenylethyl)amine [4, 5], or *N*-(2-iodobenzyl)-*N*-[2-(2-

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-iodophenyl)ethyl]amine [6] at $\lambda = 280$ nm afforded compound *VII* in low yields.

Synthesis of 5,6,7,8-tetrahydrodibenz[*c*,*e*]azocines substituted in the aromatic moiety by methoxy or methylenedioxy groups started from substituted methyl 2-formyl-2′-biphenylcarboxylate the carbaldehyde group of which reacted with nitromethane to give the corresponding 2-nitroethenyl derivative. A parallel reduction of its 2-nitroethenyl and methoxycarbonyl groups led to the 2-hydroxymethyl-2′-(2-aminoethyl)biphenyl derivative; its subsequent reaction with phosphorus tribromide gave the required azocine [7, 8].

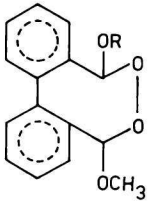
A method starting from 2-(2-bromoethyl)-2′-(bromomethyl)biphenyl and benzylamine proceeded through 6-benzyl-5,6,7,8-tetrahydrodibenz[*c*,*e*]azocine and its hydrogenolysis over palladium. Nevertheless, the low yield of the 6-benzyl derivative does not allow to exploit this method in practice [5].

All the above-mentioned procedures except those offering — according to the literature — low yields (photolysis of iodo derivatives [4—6], hydrogenolysis of 6-benzyl derivatives [5]), or those unfavourable for use on large scale (azoimide in trichloroacetic acid [2]) were reproduced. Even though yields of some synthetic steps could be improved, still the overall yield of separate synthetic routes remained low. Thus *e.g.* a modified procedure according to [1] afforded compound *VII* in a 21 % yield (per the starting phenanthrene), and according to [3] and [7, 8] in 31 % and 20 % yield, respectively.

As a result of this investigation we suggested a four- or five-step synthesis of compound *VII* from phenanthrene in a quite passable yield. It utilized the already known ozonolysis [9] of phenanthrene (*I*) to 3,8-dimethoxydibenzo[*c*,*e*]-[1,2]dioxacyclooctane (*IIb*), its transformation to methyl 2-(2-nitroethenyl)-2′--biphenylcarboxylate (*IV*), partial reduction of the nitroethenyl group to methyl 2-(2-aminoethyl)-2′-biphenylcarboxylate (*V*), followed by a base-catalyzed cyclization to 5,6,7,8-tetrahydrodibenz[*c*,*e*]azocin-5-one (*VI*) and reduction of its lactam grouping to the final compound *VII*.

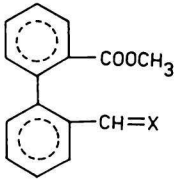
When reproducing the preparation of dioxacyclooctane derivative *IIb* from *I* according to [9] in up to a 30-times larger scale a decrease of yields and especially a worse quality of *IIb* were observed. The reason for contamination of *IIb* with the starting *I* is the low solubility of *I* in methanol at low temperatures (−20— −26 °C) needed and the fact that the product of ozonolysis *IIa* began to separate from the reaction mixture prior to the complete dissolution of the starting *I*. This problem could be solved by replacement of a part of methanol by chloroform in which *I* is much better soluble. In such a modified medium the starting *I* had become totally dissolved already after a short introduction of ozone before the ozonolysis product *IIa* started to separate. After the ozonolysis had been completed a catalytical amount of a strong inorganic acid was added to dissolve the semiacetal product of ozonolysis *IIa*;

the latter was transformed into the diacetal derivative of dioxacyclooctane *IIb*, which immediately began to separate. This synthetic step proceeded in 84 % yield, which is in line with the 82 % yield declared in [9].



IIa R = H

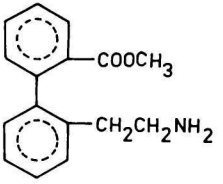
IIb R = OCH_3



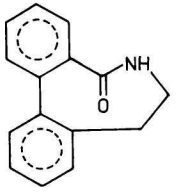
IIIa X = N–C_4H_9

IIIb X = N–$CH_2CH{=}CH_2$

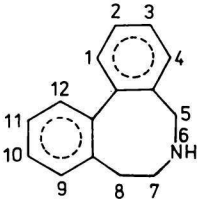
IV X = CH–NO_2



V



VI



VII

The dioxacyclooctane derivative *IIb* could be transformed into 2-(2-nitroethenyl) derivative *IV* in various ways. At hand is the conversion of *IIb* to methyl 2-formyl-2′-biphenylcarboxylate according to [10] in a 75 % yield and transformation of the carbaldehyde grouping into a nitroethenyl one according to [8]; compound *IV* was thus obtained in 82—86 % yield. As ascertained, derivative *IIb* need not be converted into the above-mentioned 2-formyl derivative, since it was sufficient to heat it with some alkylamine, *e.g.* with butyl- or allylamine and the Schiff's base *IIIa*, *IIIb* formed was directly reacted with nitromethane to yield the required 2-(2-nitroethenyl) derivative *IV* in *ca.* 92 % yield per compound *IIb*. This modification made it possible to rise the yield of compound *IV* by 6—8 %.

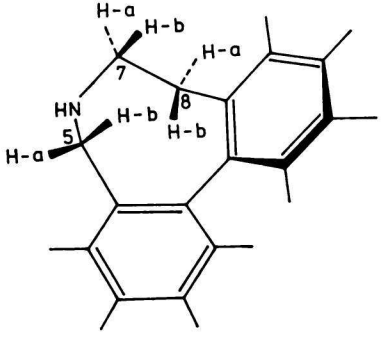
Unlike to procedures for preparation of compound *VII* described so far, we reduced the derivative *IV* only partially to methyl 2-(2-aminoethyl)-2′-biphenylcarboxylate (*V*) by a low-pressure hydrogenation over palladium in acetic acid in the presence of sulfuric acid in approximately 83 % yield.

The next synthetic step concerned the preparation of azocin-5-one derivative *VI*. This lactam originated by a mere heating of 2-(2-aminoethyl) ester *V* Cyclization to the lactam *VI* can be accelerated by adding a base, *e.g.* an alcoholate. Reflux with sodium methoxide in methanol for 1 h is sufficient for a virtually quantitative cyclization (*ca.* 96 % yield).

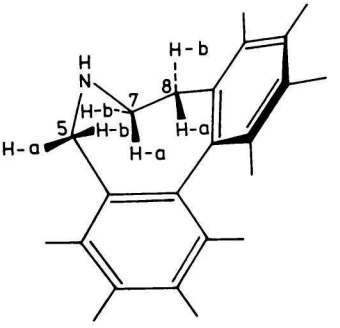
The last synthetic step was characterized by reduction of the azocin-5-one derivative *VI* to the final product *VII*; this procedure was done with a mixture of lithium hydridoaluminate and aluminium chloride or with sodium bis(2--methoxyethoxy)hydridoaluminate. The latter procedure was proved more advantageous for its 92 % yield of azocine *VII*. The last two steps of this synthesis could be unified, *i.e.* the excess of lithium bis(2-methoxyethoxy)hydridoaluminate made it possible to get the azocine *VII* from the 2-(2-aminoethyl) ester *V* in 80 % yield. The course of this reaction could be explained as follows: the complex hydridoaluminate reacted with the acidic hydrogen atoms of the amino group of compound *V* to form an amide anion which accelerated cyclization to the azocin-5-one derivative *VI*, which was then reduced to the azocine *VII*. Both procedures — this with isolation and that without isolation of azocin-5-one *VI* — are virtually equivalent as far as their yields are concerned. The difference is, however, in the purity of compound *VII*. In the simplified procedure the excess of sodium bis(2-methoxyethoxy)hydridoaluminate attacked the methoxycarbonyl group of derivative *V* in a moderate manner to form 2-(2-aminoethyl)-2′-(hydroxymethyl)biphenyl which contaminated the final azocine *VII*. The overall yield of compound *VII* was 49 % per the starting substance *I*.

Compounds *IV*, *V*, and *VI* have not been described as yet. Their structure was corroborated by elemental analyses, mass, infrared and ^{1}H NMR spectra. The identity of products *VII* obtained according to experiments described in Experimental and according to literature was evidenced by comparing their ^{1}H NMR spectra, R_f values, and melting points. Signals of protons at C-5, C-7, and C-8 could be ascribed owing to a ^{1}H and ^{13}C NMR apparatus of a good resolution power and thereby the conformation of compound *VII* was solved. To assign unambiguously the proton signals prerequisite for solution of conformation the ^{13}C NMR signals of *VII* were first analyzed: signals of three CH_2 carbons were found at δ: 50.9, 49.6, and 37.4. Signals at higher chemical shifts belonged — regarding the bonds to nitrogen — to carbons in positions 5 and 7, whilst the signal at $\delta = 37.4$ to C-8. Selective decoupling of the proton at $\delta = 2.26$ resulted in simplification of multiplicity of C-8 to a doublet, which means that one of its protons was decoupled. The remaining signals in the ^{1}H NMR spectrum were ascribed respecting their proton—proton coupling constants. Controversial remained the mutual resolution between signals of *pro-R* and *pro-S* hydrogen atoms of prochiral CH_2 groups of C-5, C-7, and C-8.

The data for chemical shifts and coupling constants could be interpreted in two ways: *a*) say, the signals at $\delta = 3.36$ and 2.79 belong to H-7a and H-7b, respectively and signals at $\delta = 2.78$ and 2.26 to H-8a and H-8b, respectively. Then the conformation of the eight-membered ring, in accord with the coupling constant values measured, is denoted in the following formula as *A*. Protons H-5b and H-7b of this conformer are shielded by both benzene rings and consequently, their signals in the ^{1}H NMR spectrum appeared in a higher field than those of their geminal counterparts.



A



B

Conformation *B* reflects the opposite assignment of protons at prochiral centra C-7 and C-8. Contrary to this conformation is the assignment of protons at C-8, which should be, due to magnetic anisotropy of the benzene ring, quite reverse (interpretation *B*).

Decision between the afore-mentioned possibilities brought forward the ^{1}H—^{1}H NOE differential experiment [11]. The signal at $\delta = 3.16$ belonging to H-5b proton (having lower chemical shifts than H-5a in both conformations due to shielding by a more remote benzene ring) was saturated which caused a 2.4 % NOE effect at $\delta = 2.79$; this is only possible when this signal belonged to H-7b and the eight-membered ring would be in conformation *A*. The dihedral angle between both benzene rings is in this case approximately 60° (conformation *B* requires the angle up to 80°).

The UV spectrum of compound *VII* disclosed an absorption band at $\lambda =$ = 238 nm associated with a biphenyl grouping; this value agreed with that of diethyl dibenzo[*c*,*e*]cyclooctane-6,7-dicarboxylate [12], thus evidencing the same dihedral angle of both compounds. The bulky ethoxycarbonyl substituents of diethyl dibenzo[*c*,*e*]cyclooctanedicarboxylate in positions 6 and 7 virtually exclude the existence of the conformer *B*, this being, however, in line with the results of the ^{1}H NMR spectrum analysis of compound *VII*.

Experimental

The starting phenanthrene and further chemicals used were commercially available (Lachema, Brno; Fluka, Buchs). Ozone was generated from medicinal oxygen containing 5 % of carbon dioxide in a Fischer Ozonizer. The melting points were estimated on a Kofler micro hot-stage, the electron impact mass spectra were measured at 70 eV and at the emission current of 100 μA with an AEI MS 902 S (Manchester) apparatus and the IR spectra with a model 559 (Perkin—Elmer) instrument. The ^{1}H NMR spectra of compounds *IV—VI* and *VII* in $CDCl_3$ containing tetramethylsilane as an internal standard were recorded with Tesla 487 C (80 MHz) and Bruker AM 300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) instruments, respectively. The purity of products was checked by thin-layer chromatography on Silufol 254 UV sheets in chloroform—acetone (φ_r = = 10 : 1).

3,8-Dimethoxydibenzo[c,e][1,2]dioxacyclooctane (IIb)

A mixture consisting of ozone and oxygen (flow rate of O_3 6 g h^{-1}) was introduced through a sintered glass filter into a solution of *I* (133.5 g; 0.7 mol) in methanol (550 cm^3) and chloroform (550 cm^3) at −26—−20 °C till the solution of potassium iodide through which the gas outflowed turned brown-red with the unconsumed ozone (7 h). Concentrated hydrochloric acid (3 cm^3) was then added and the mixture was allowed to stand at room temperature for 2 h and at −5—0 °C overnight. The separated intermediate *IIb* was filtered off, washed with cold methanol (100 cm^3) and to the filtrate, concentrated to 200 cm^3 under reduced pressure, methanol (200 cm^3) was added. The second portion of *IIb* separated by standing in the cold was combined with the first one and the product was crystallized from acetone. Yield = 172.3 g (84 %), m.p. = 179—182 °C (Ref. [9] gives m.p. = 178—181 °C).

Methyl 2-(2-nitroethenyl)-2'-biphenylcarboxylate (IV)

Butylamine (36.6 g; 0.5 mol) was added to the stirred suspension of the intermediate *IIa* (108.8 g; 0.4 mol) in anhydrous ethanol (240 cm^3) at 70—75 °C. The mixture was then refluxed with stirring for 1 h, cooled and while permanently stirred nitromethane (76 cm^3; 1.4 mol) and acetic acid (99 %, 120 cm^3; 2.0 mol) were added at 20—25 °C. Stirring at room temperature was continued for 5 h and the intermediate *IV* crystallizing on standing during the night was filtered off and crystallized from acetic acid. Yield = 52.0 g (92 %), m.p. = 100—101 °C. For $C_{16}H_{13}NO_4$ (M_r = 283.3) w_i(calc.): 67.84 % C, 4.62 % H, 4.94 % N; w_i(found): 67.95 % C, 4.70 % H, 5.05 % N. Mass spectrum, *m/z*: 283 ($M^{+\bullet}$). IR spectrum ($CHCl_3$), $\tilde{\nu}$/cm^{-1}: 1720 (C=O ester), 1521 and 1340 (NO_2). ^{1}H NMR spectrum ($CDCl_3$), δ: 6.5—7.1 (m, 8H, H_{arom}), 7.75 (d, 1H, O_2N—CH=), J_{AB} = 13.3 Hz, 7.50 (d, 1H, Ar—CH=), J_{AB} = 13.3 Hz.

Methyl 2-(2-aminoethyl)-2'-biphenylcarboxylate (V)

Nitroethenyl derivative *IV* (20.3 g; 72 mmol) dissolved with cooling in acetic (99 %, 400 cm^3) and sulfuric (96 %, 33.9 cm^3; 318 mmol) acids was hydrogenated over palladium on charcoal (10 % Pd, 4.0 g) in an autoclave at $p = 0.4$ MPa, till the calculated amount of hydrogen (6 dm^3) was consumed (30—60 min). The catalyst was filtered off, the acids were neutralized with sodium hydroxide (8 %) at $\theta_{max} = 22$ °C with stirring. Sodium sulfate, separated during the 1 h standing was filtered off, the filtrate was concentrated under reduced pressure and the residue (*V* $1/2\,H_2SO_4$) was dissolved in water (100 cm^3). Impurities were extracted from the aqueous solution with benzene (100 cm^3), the aqueous layer was made alkaline with 8 % sodium hydroxide and the precipitated base *V* was taken into ether (200 cm^3). The ethereal solution was dried with potassium carbonate and the solvent was evaporated under diminished pressure to give an oily product, which was dried at 60 °C (16 Pa); the oil turned spontaneously into a crystalline mass on standing, m.p. = 20—25 °C. Yield = 15.4 g (83 %). A sample for analysis was distilled at 152 °C (8 Pa). For $C_{16}H_{17}NO_2$ ($M_r = 255.3$) w_i(calc.): 75.27 % C, 6.71 % H, 5.49 % N; w_i(found): 75.12 % C, 6.20 % H, 5.22 % N. Mass spectrum, *m/z*: 255 ($M^{+\bullet}$). IR spectrum (nujol), $\tilde{\nu}/cm^{-1}$: 1740 (C=O ester), 3330 (NH_2). ^{1}H NMR spectrum ($CDCl_3$), δ: 7.0—8.0 (m, 8H, H_{arom}), 3.61 (s, 3H, $COOCH_3$), 3.0—4.0 (m, 4H, $2 \times CH_2$), 1.70 (s, 2H, NH_2).

Chloride of compound *V*, prepared from methanolic hydrogen chloride, was crystallized from ethanol—ether; m.p. = 123—126 °C. For $C_{16}H_{18}ClNO_2$ ($M_r = 291.8$) w_i(calc.): 65.86 % C, 6.22 % H, 4.80 % N; w_i(found): 65.54 % C, 6.20 % H, 4.40 % N.

5,6,7,8-Tetrahydrodibenz[c,e]azocin-5-one (VI)

Aminoethyl ester *V* (20.8 g; 80 mmol) was refluxed in methanolic sodium methoxide (50 cm^3, 1.0 g Na; 44 mmol) for 1 h, the mixture was cooled, neutralized with dilute 20 % formic acid and the product which crystallized on standing was recrystallized from ethanol. Yield = 8.6 g (96 %), m.p. = 254—255 °C. For $C_{15}H_{13}NO$ ($M_r = 223.3$) w_i(calc.): 80.69 % C, 5.87 % H, 6.28 % N; w_i(found): 80.35 % C, 5.81 % H, 6.28 % N. Mass spectrum, *m/z*: 223 ($M^{+\bullet}$). IR spectrum (KBr), $\tilde{\nu}/cm^{-1}$: 1650 (C=O lactam). ^{1}H NMR spectrum ($CDCl_3$), δ: 6.9—7.8 (m, 8H, H_{arom}), 3.27 (s, 1H, NH), 3.09 (m, 2H, H-8), 2.73 (m, 2H, H-7).

5,6,7,8-Tetrahydrodibenz[c,e]azocine (VII)

Method A. Azocin-5-one *VI* (20.5 g; 92 mmol) was poured into a mixture of sodium bis(2-methoxyethoxy)hydridoaluminate (70 % in toluene, 60 g; 0.23 mol) and toluene (300 cm^3) with stirring. Due to exothermic reaction the temperature rose to 50—60 °C and the stirring was continued at 90 °C for 2 h. The mixture was cooled to 5—10 °C and the excess of the reduction agent was decomposed by adding ice-cold water (10 cm^3). Further water was added till formation of the white precipitate ceased. The content was

thoroughly mixed, the toluene layer was separated, washed with dilute 10 % hydrochloric acid (100 cm^3) and the chloride of product *VII* having been allowed to crystallize was filtered off and suspended in benzene (200 cm^3) to which 4 % sodium hydroxide (140 cm^3) was introduced. After the base *VII* was completely dissolved in the benzene layer (*ca.* 30 min) the solvent was dried with potassium carbonate, distilled off under diminished pressure and the residue crystallized from acetone. Yield = 17.4 g (92 %), m.p. = = 119—120 °C; Ref. [2] reports m.p. = 114—115 °C.

Method B. Anhydrous aluminium chloride (3.3 g; 25 mmol) in ether (50 cm^3) was added into a stirred suspension of lithium hydridoaluminate (2.8 g; 75 mmol) in tetrahydrofuran (120 cm^3) at room temperature. After 10 min azocin-5-one *VI* (11.0 g; 50 mmol) was introduced and the stirred mixture was refluxed for 2 h. Stepwise, water-saturated benzene (100 cm^3), ice-cold water (10 cm^3), and 8 % sodium hydroxide (25 cm^3) were added to the stirred and cooled mixture. The organic layer was separated, dried with potassium carbonate, the solvent was removed under reduced pressure and the crude product was crystallized from acetone. Yield = 8.6 g (82 %), m.p. = 116—118 °C.

Method C. Sodium bis(2-methoxyethoxy)hydridoaluminate (70 % in toluene, 11.5 g; 40 mmol) dissolved in toluene (25 cm^3) was added to a stirred solution of aminoethyl ester *V* (7.8 g; 35 mmol) in toluene (60 cm^3) at 60—75 °C. The mixture was stirred for additional 30 min, when a double amount of the reducing agent was added; stirring and heating at 85—95 °C were continued for 2 h. The mixture was cooled, the unreacted hydridoaluminate was decomposed with ice-cold water and further water (*ca.* 20 cm^3) was dropped in till a white precipitate arose. The toluene layer was separated, washed with 12 % HCl (30 cm^3) and left to stand at room temperature. The crystalline chloride of the final product *VII* was suction-filtered and dried. Yield of *VII* HCl was 6.8 g (80 %), m.p. = 302—305 °C; Ref. [2] reported m.p. = 290—291 °C. ^{1}H NMR spectrum ($CDCl_3$), δ: 6.95—7.38 (m, 8H, aromatic H-1, H-2, H-3, H-4, H-9, H-10, H-11, H-12), 3.90 (d, 1H, H-5a), $J_{H\text{-}5a,\,H\text{-}5b}$ = 14.0 Hz, 3.36 (ddd, 1H, H-7a), $J_{H\text{-}7a,\,H\text{-}7b}$ = 13.6 Hz, $J_{H\text{-}7a,\,H\text{-}8a}$ = 6.5 Hz, $J_{H\text{-}7a,\,H\text{-}8b}$ = 1.6 Hz, 3.16 (d, 1H, H-5b), 2.79 (ddd, 1H, H-7b), $J_{H\text{-}7b,\,H\text{-}8b}$ = = 10.8 Hz, $J_{H\text{-}7a,\,H\text{-}8b}$ = 1.1 Hz, 2.78 (ddd, 1H, H-8a), $J_{H\text{-}8a,\,H\text{-}8b}$ = 13.8 Hz, 2.26 (ddd, 1H, H-8b). ^{13}C NMR spectrum ($CDCl_3$), δ: 140.9, 140.9, 140.2, 139.9 ($4 \times C_{quaternary}$), 129.4, 129.3, 129.2, 129.1, 128.1, 128.0, 126.9, 125.8 ($8 \times C_{arom}$), 50.9 (C-5), 49.6 (C-7), 37.4 (C-8).

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Translated by Z. Votický