γ-Alkynyl oxime cyclization: an easy route to a new heteropolyring: 3a,8a-butano-3a,8a-dihydro-3*H*-benzo[4,5]furo[2,3-*b*]pyrrole-1-oxide

Jean-Louis Avril,[a] Bernard Marçot,[a] Michel Coquillay,[b] Colette De Rango,[b] Henri Moskowitz[a] and Joëlle Mayrargue*[a]

[a] *Laboratoire de Chimie Organique CNRS (UPRES-A BIOCIS 8076), Faculté de Pharmacie, rue J.-B. Clément, 92296 Châtenay-Malabry cedex, France.*
[b] *Laboratoire de Physique CNRS (ERS 582), Faculté de Pharmacie, rue J.-B. Clément, 92296 Châtenay-Malabry cedex, France.*

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Hydroxylamine reacts with 2-(2,3-dimethoxyphenyl)-2-propynylcyclohexanone **1** and leads, not to the expected oxime, but to a *N*-hydroxyaminonitrone **5**, according to a reverse-Cope or a 1,3-azaprotiocyclotransfer (APT) mechanism. The deprotection of the phenol functions by a $AlCl_3$–Me_2S mixture is accompanied by a cyclisation resulting from attack of the nitrone function, leading to new heteropolyrings **11** and **12**, derived from 3*a*,8*a*-butanobenzo[4,5]furo[2,3-*b*]pyrrole. The mechanisms are discussed.

Résumé. Cyclisation d'oximes γ-acétyléniques: un accès facile à un nouvel hétérocycle polycondensé, le 3a, 8a-butano-3a,8a-dihydro-3*H*-benzo[4,5]furo[2,3-*b*]pyrole-1-oxyde. L'hydroxylamine réagit avec la 2-(2,3-diméthoxyphényl)-2-propynylcyclohexanone **1** pour conduire non pas à l'oxime attendue, mais à une *N*-hydroxyaminonitrone **5** selon un mécanisme de type "reverse-Cope" ou APT. La déprotection des fonctions phénol de ce dérivé par le mélange $AlCl_3$–Me_2S s'accompagne d'une cyclisation par attaque de la fonction nitrone et permet d'obtenir facilement de nouveaux hétérocycles polycycliques **11** et **12**, dérivés des 3*a*,8*a*-butanobenzo[4,5]furo[2,3-*b*]pyrroles.

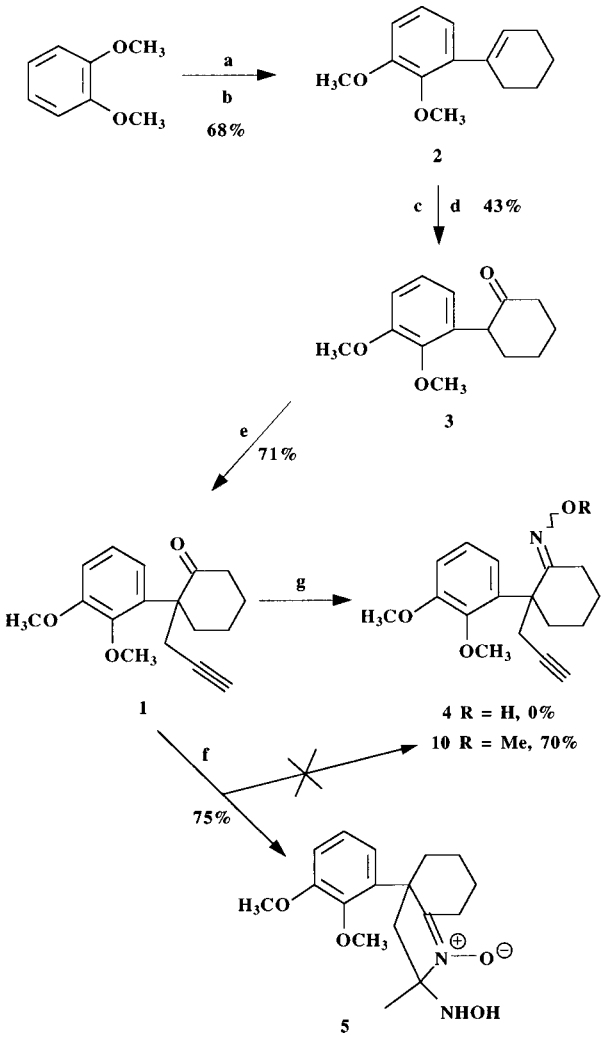
In our search for morphinic analogs, we have synthesized various benzofurane compounds starting from 1-allyl(2,3-dimethoxyphenyl)cyclohexene.[1,2] Starting from 2-(2,3-dimethoxyphenyl)-2-propynylcyclohexanone **1**, we have succeeded in the synthesis of a new heteropolyring derived from 3a,8a-butano-3a,8a-dihydro-3*H*-benzo[4,5]furo[2,3-*b*]pyrrole. To our knowledge, this structure has never been described and only a few references quote the synthesis of 3*H*-benzo[4,5]furo[2,3-*b*]pyrroles.[3] We describe herein a new convenient and efficient method of preparing this type of compound from a common starting material.

The ketone **1** was prepared from 1,2-dimethoxybenzene (veratrole) according to Scheme 1.[4] Condensation of 2,3-dimethoxyphenyllithium with cyclohexanone yielded 1-(2,3-dimethoxyphenyl)cyclohexan-1-ol. Its dehydration was performed without purification by oxalic acid treatment in boiling benzene to yield 68% of 1-(2,3-dimethoxyphenyl)cyclohexene **2**. Hydroboration of **2**, followed by basic hydrogen peroxide oxidation, gave a crude product that was oxidized with pyridinium chlorochromate in CH_2Cl_2. 2-(2,3-Dimethoxyphenyl) cyclohexanone **3** was obtained in 43% yield and its reaction with propargyl-bromide and NaH in refluxing benzene gave **1** in 71% yield.

Ketone **1** was unreactive and failed to give the monooxime **4** under normal conditions. A similar lack of reactivity towards various nucleophiles was reported by Newman and Mosly[5] and by Horning and Finelli[6] for 2-(2,3-dimethoxyphenyl)-2-ethylcyclohexanone. Only the treatment of ketone **1** with a large excess of hydroxylamine in refluxing ethanol for 20 h led, after the usual workup, to the unexpected bicyclic nitrone **5** in 75% yield (Scheme 1). The structure of **5** was determined on the basis of elemental analysis, which indicated the presence of two nitrogen atoms, and NMR spectral data, which evidenced the formation of only one stereoisomer. ^{1}H and ^{13}C NMR data demonstrated: (*i*) the disappearance of the triple bond, (*ii*) the advent of a methyl group (singlet at 1.3 ppm in ^{1}H NMR, quadruplet at 20.8 ppm in ^{13}C NMR), and (*iii*) the advent of a quaternary carbon strongly deshielded at 91.5 ppm. These data fit with structures corresponding to the cyclized products **A** or **B** (Scheme 2), resulting from the attack by two molecules of hydroxylamine.

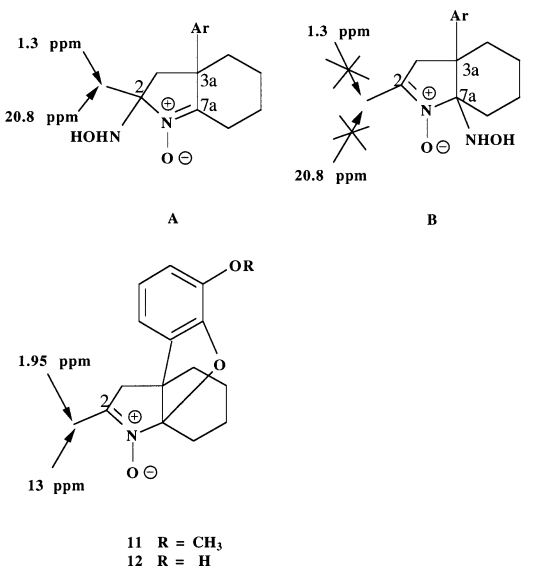
We eliminated structure **B** for the following reasons. The methyl group created by cyclization exhibits a ^{1}H NMR signal at 1.3 ppm, which is not in accordance with a methyl supported by a carbon double-bonded to a nitrogen. The ^{13}C NMR signal of one of the two quaternary carbons (2 or 7a) is missing and neither changes in solvent ($CDCl_3$, C_6D_6, CD_3OD), nor temperature variations, nor the addition of a relaxing agent [chromium (III) acetylacetonate] were able to show its presence. The signal at 91.5 ppm was assigned to the carbon bearing the two nitrogen atoms and the expected and missing signal (between 140 and 150 ppm) should correspond to carbon 7a of **A** or 2 of **B**. The carbon 2 of **B** has no obvious reason to have difficulty to relax, whereas the carbon 7a of **A** is near the quaternary center 3a bonded to the phenyl ring. Moreover, the structures **11** and **12**, analogues to **B** and proven by X-ray diffraction (see below) exhibit methyl signals at 1.95 and 13 ppm.

Although such an evolution has never been described as a result of a reaction between hydroxylamine and γ-acetylenic ketones, it is nevertheless close to cyclizations described by Pradhan *et al.*[7] when δ-acetylenic oximes are treated with sodium borohydride or by Grigg *et al.*[8] when these oximes are treated with *N*-methylmaleimide (NMM). These authors invoke an intermediate nitrone (Scheme 3) transformed into hydroxylamine by $NaBH_4$ and into a bicyclic compound by NMM. This nitrone could arise *via* a mechanism assimilated by Ciganek[9] to a "reverse-Cope" one and called by Grigg *et al.*[8] a "1,3-azaprotiocyclotransfer" (APT). Although convincing circumstantial evidence was provided that ***E*** was formed

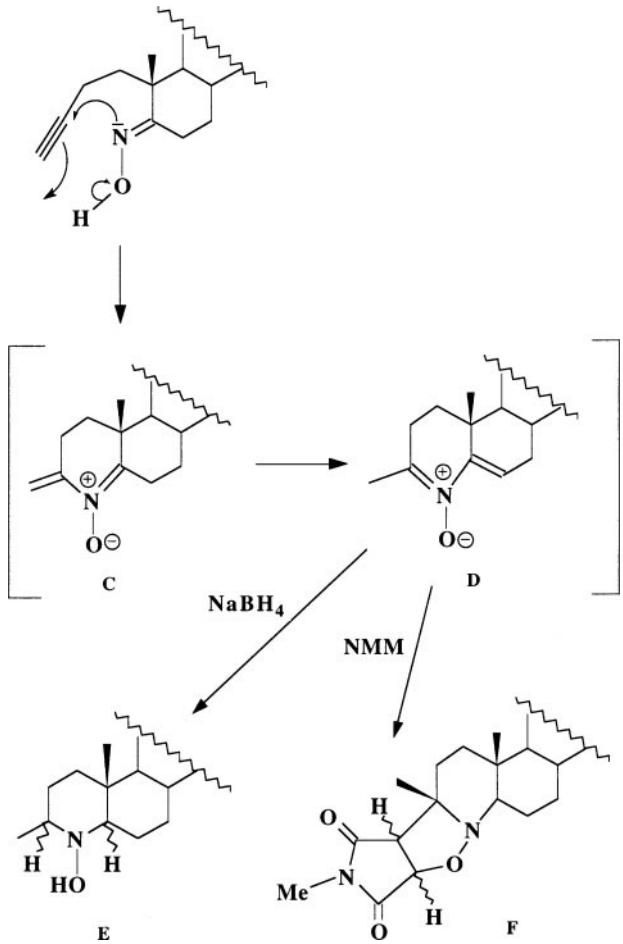


Scheme 1 **a:** Bu^{n}Li, then cyclohexanone; **b:** $(COOH)_2/\Delta$/benzene; **c:** BH_3/THF, then $NaOH/H_2O_2$; **d:** PCC/CH_2Cl_2; **e:** NaH/benzene, then propargyl bromide/Δ; **f:** H_2NOH, $HCl/CH_3COONa/EtOH/\Delta$; **g**: H_2NOMe, $HCl/CH_3COONa/EtOH/\Delta$.

via **C** to **D**, nitrone intermediates were not detected by Pradhan *et al.*,[7] while the isolation of **F** by Grigg *et al.*[8] proved the existence of the intermediate **D**, but not the passage *via* the intermediate **C**. Moreover, Grigg *et al.*[8] reported that five-membered ring formation had not been observed in oxime–alkyne APT processes because of the higher strain energy of the ring system.



Scheme 2

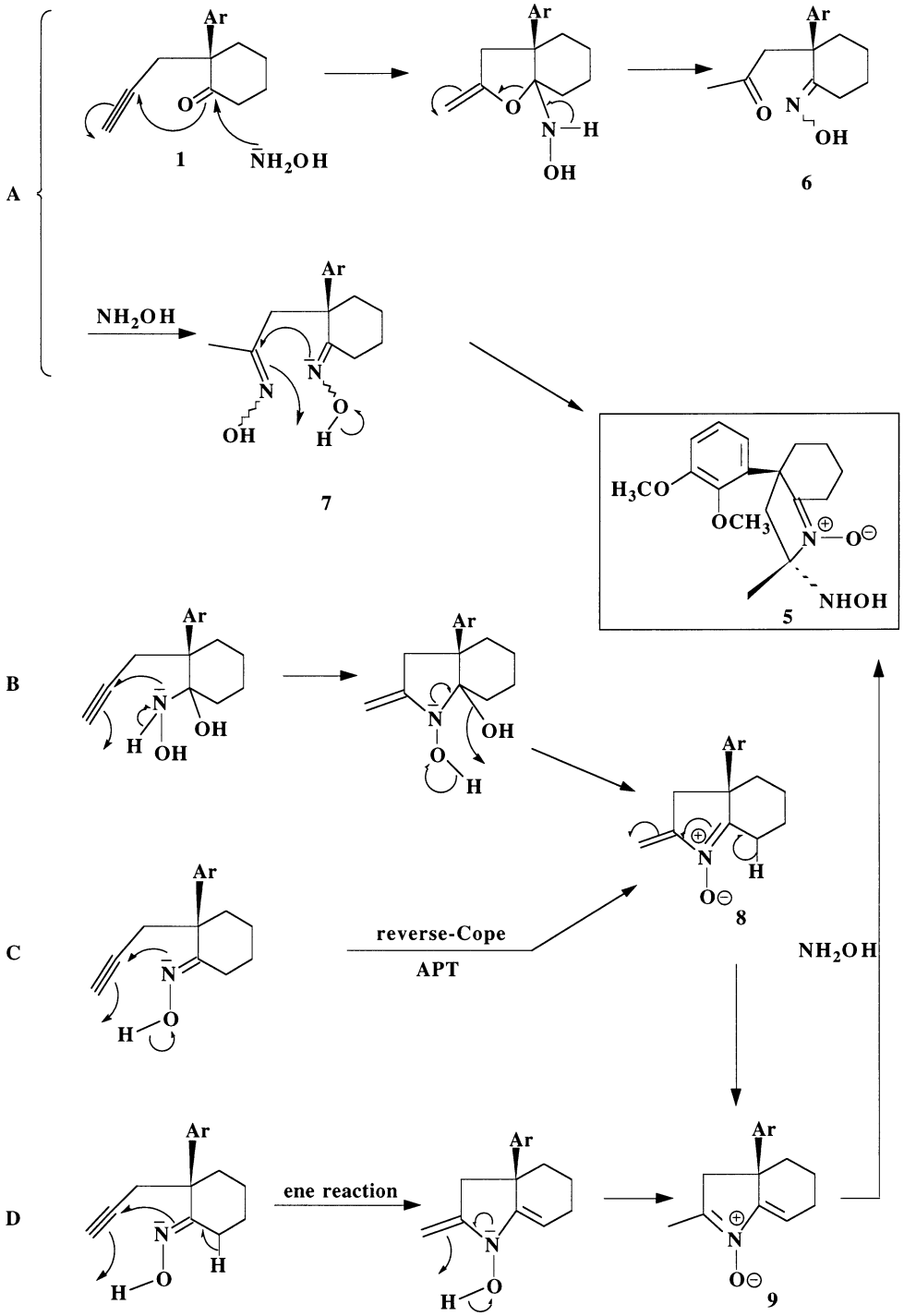


Scheme 3

Thus, to explain the isolation of **5**, we considered all the mechanisms able to create it from **1**. Four mechanisms can be envisaged (Scheme 4). According to pathway A, intermediate **6** could be formed by hydration of the triple bond during the attack of hydroxylamine on the carbonyl group. We previously showed[10] that such hydration of an acetylenic bond could take place in alkaline solution. **5** could then come from rearrangement of the dioxime **7** arising from **6**.

In pathway B, the nitrogen atom of the hemi-aminal arising from the addition of hydroxylamine to the carbonyl carbon atom should attack the triple bond, leading to a 2-methylenazolidine, which by losing one water molecule could give rise to the azadienic structure **8**. A second attack of hydroxylamine could convert **8** into **5**. Pathway C shows that the same intermediate **8** could be obtained using a reverse-Cope/APT mechanism as described in Scheme 3. However, in both cases it is unlikely that the second hydroxylamine molecule would attack at the correct position to give **5**. The formation of **5** should then follow an initial rearrangement of **8** into **9**, which appears to be the privileged intermediate on which the attack of hydroxylamine should take place *anti* to the aromatic ring, leading to only one diastereomer. Finally, in pathway D, an ene reaction should lead directly to the azadienic structure **9**, isomer of **8** and precursor of **5**.

We discarded pathway A because when an excess of *O*-methylhydroxylamine was reacted with **1**, only the monooximes **10** ($Z + E$, see Scheme 1) were isolated despite using large quantities of reactants and prolonged heating. If a ketone analogous to **6** was formed, the reaction would give a dioxime analogous to **7**. Moreover, **5** should be obtained as a mixture of diastereomers. Pathways B, C and D imply the departure of a proton from carbon 7 and isotopic labeling did not make it possible to differentiate among these three possibilities. In order to get more data to resolve this problem, we



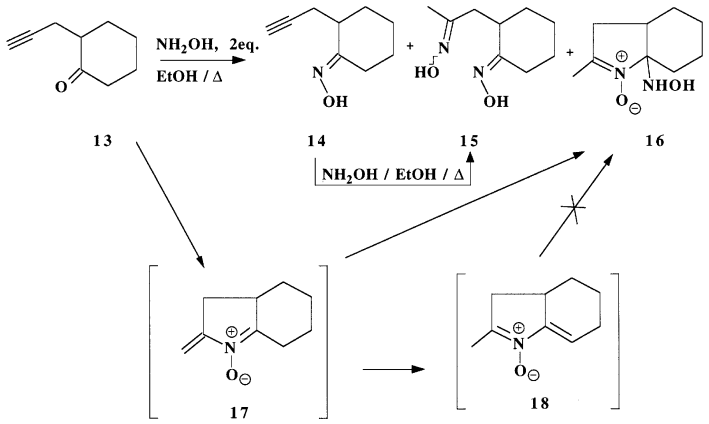
Scheme 4

prepared a simplified model compound **13** devoid of an aromatic ring (Scheme 5). When reacted with an excess of hydroxylamine under the same conditions as **1**, **13** yielded oxime **14**, dioxime **15** and a compound to which we ascribe the structure **16**. This latter compound exhibits signals at 1.8 ppm (^{1}H NMR) and 13 ppm (^{13}C NMR) for the methyl group in position 2 similar to the methyl signals in **11** and **12**. If we assume that the mechanism leading from **13** to **16** is identical with the one leading from **1** to **5**, the fact that **14**, when heated for a long time with an excess of hydroxylamine, leads to dioxime **15** allows us to definitively exclude the pathways A and B.

Of the two intermediates **17** and **18** (Scheme 5), which are consistent with pathways C or D, only the less stable intermediate **17** bearing an exocyclic methylene is able to give **16**. This excludes therefore pathway D. We therefore conclude that this kind of cylization proceeds *via* a 1,3-azaprotiocyclotransfer (pathway C). The intermediate **8**, bearing a bulky aromatic substituent, would isomerize into **9** prior to hydroxylamine addition on carbon 2, while the intermediate **17** would react immediately with hydroxylamine to give **16**. It is then likely that the observed formation of dioxime **15** proceeds via **16** with subsequent ring opening. In contrast, **5** is stable and no trace of dioxime can be detected in this reaction.

To explore the reactivity and utility of **5**, we studied this compound under various conditions. After treatment by $AlCl_3$–Me_2S, a mixture of the 3a,8a-butano-3a,8a-dihydro-3*H*-benzo[4,5]furo[2,3-*b*]pyrrole-1-oxides **11** and **12** was obtained in 76% yield and in a 38 : 62 ratio. The proposed mechanism is drawn in Scheme 6.

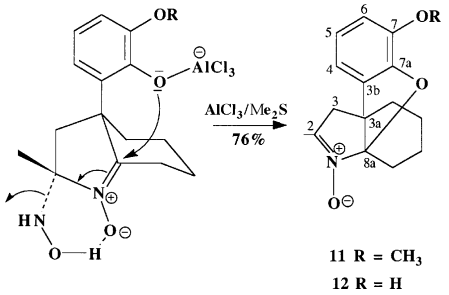
The ^{1}H NMR, ^{13}C NMR and elemental analysis were consistent with the proposed structures of the products. The structure of the well-crystallized compound **12** was also confirmed by X-ray diffractometry[11,12,13] (Fig. 1).



Scheme 5

The molecular conformation consists of three moieties linked together through the C(3a)–C(8a) saturated bond. The benzofuran skeleton is quite planar with deviations of 0.005 Å from the least squares plane when C8a is excluded [deviation of 0.350(3) Å]. The pyrrole ring without C3a is also planar with a mean deviation of 0.022 Å, the atom C3a being out-of-plane by 0.384(3) Å. The dihedral angle between these planes is 84.6° The fused cyclohexane ring adopts a chair conformation with bond angles in the range 107.3°–114.7° except for C(3a)–C(8a)–C(9) (118.3°) and C(3b)–C(3a)–C(8a) (99.6°), which highly deviate from the ideal sp^3 value, reflecting the molecular strain. Two symmetrical molecules are strongly paired as a dimer around a center of symmetry by a hydrogen bond O(7)–H(7)···O(1) [2.618(3) Å] between the hydroxyl group attached to the phenyl ring and the *N*-oxide of the pyrrole ring. The phenyl rings of adjacent dimers are stacked by a distance of 3.55 Å between their mean planes.

In this work, we showed the possibilities of spontaneous cyclization of γ-acetylenic oximes. We proved that this cyclization proceeds *via* an APT mechanism already described by Grigg *et al.*[8] and by Pradhan *et al.*[7] We also succeed in isolating addition compounds of hydroxylamine on the two kinds of postulated nitrone intermediates. These results extend and corroborate the previous results of thse authors. Moreover, we used the reactivity of these nitrones to easily synthesize a new polyring heterocycle.



Scheme 6

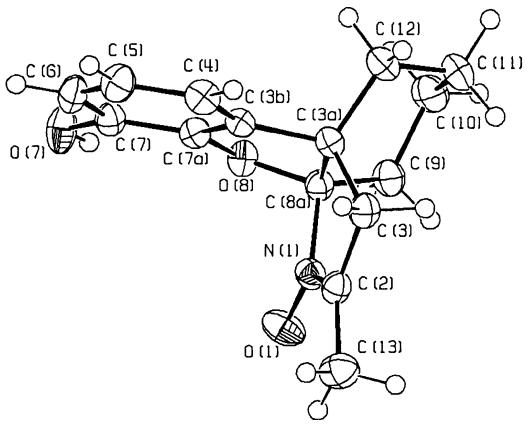


Fig. 1 View of compound **12** (non-H atom displacement ellipsoids are drawn at the 50% probability level).[13]

Experimental

^{1}H NMR spectra were recorded at 200 MHz with a Brüker WP-200 spectrometer in $CDCl_3$ using TMS as an internal reference. Chemical shifts are expressed in ppm. ^{13}C NMR spectra were recorded at 50 MHz with a Brüker WP-200 spectrometer in $CDCl_3$, adopting δ 77.00 for the central line of $CDCl_3$. Assignments were aided by the J-mode technique. Reactions were monitored by TLC on silica gel 60 F254 (Merck). Column chromatography was performed on silica gel 60 (63–200 mesh or 40–63 mesh). Elemental analyses were performed on a Perkin Elmer 240 apparatus.

Syntheses

2-(2,3-Dimethoxyphenyl)cyclohexanone. Using Bergmann *et al.*'s method,[4] but without isolation of the intermediate alcohol, we obtained 1-(2,3-dimethoxyphenyl)cyclohexene with a 68% yield. This compound was treated with borane/NaOH/H_2O_2 and the crude product was directly oxidized by pyridinium chlorochromate[14] to give **1** (43%).

2-Propargyl-2-(2,3-dimethoxyphenyl)cyclohexanone 1. A solution of 2.5 g (10 mmol) of 2-(2,3-dimethoxyphenyl)cyclohexanone in 50 mL of anhydrous benzene was added dropwise to 1 g (25 mmol) of a 60% sodium hydride suspension in refluxing benzene (50 mL) under argon. After stirring overnight, the reaction mixture was treated with propargyl bromide (3 g, 25 mmol) and refluxed for 8 h. The mixture was then cooled and 100 mL of water were cautiously added. Workup in the usual manner of the benzene layer afforded an oil, which was chromatographed on silica gel (ethyl acetate–hexane 1 : 9) to give 2 g of **1** (71%). ^{1}H NMR ($CDCl_3$) : δ 7.0–6.9 (2m, 3H, ArH), 3.85 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 2.9 (m, 1H), 2.75 and 2.45 (2dd, J_1 = 2.6 Hz, J_2 = 17.3 Hz, 2H), 2.4 and 2.2 (2m, 2H), 1.9 (m, 1H), 1.85 (t, J = 2.6 Hz, 1H), 1.6 (m, 4H). ^{13}C NMR ($CDCl_3$) : δ 211.0 (C=O), 152.6 (C3′), 146.2 (C2′), 134.1 (C1′), 123.1 (C5′), 120.1 (C6′), 111.4 (C4′), 81.1 (C≡), 71.0 (≡CH), 60.0 (OCH_3), 55.5 (OCH_3), 54.0 (C2), 39.7, 37.4, 29.5, 28.0 and 21.5. (5 CH_2). Anal. calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 75.06; H, 7.44%.

2-(Hydroxyamino)-2-methyl-3a-(2,3-dimethoxyphenyl)-3,3a, 4,5,6,7-hexahydro-2*H*-indole-1-oxide 5. Ketone **1** (1.36 g, 5 mmol) was heated with an excess of hydroxylamine hydrochloride (1 g, 15 mmol) and sodium acetate (1.23 g, 15 mmol) in refluxing ethyl alcohol (40 mL) for 10 h. Hydroxylamine hydrochloride (1 g) and sodium acetate (1.23 g) were added again and the mixture was refluxed for another 10 h. After evaporation of the solvent, the mixture was extracted with ether. Workup in the usual manner and purification by chromatography on silica gel (dichloromethane–methanol 9 : 1) afforded **5** as a white amorphous solid (1.2 g, 75%). ^{1}H NMR ($CDCl_3$) : δ 6.95 (dd, H6′), 6.85 (d, H4′), 6.6 (m, H5′), 3.8 (s, 6H, $2OCH_3$), 3.25 (br d, 1H), 2.8 (m, 1H exchangeable), 2.7 (m, 1H), 2.2 (m, 2H), 1.8 (m, 2H), 1.55 (m, 3H), 1.3 (m, 1H + CH_3). Remark: all signals were broadened, especially H5′ at 6.6 ppm and CH_3 at 1,3 ppm. Only one exchangeable proton was observed. ^{13}C NMR ($CDCl_3$) : δ143.3 (C3′), 147.1 (C2′), 136.8 (Cl′), 123.1 (C5′), 120.1 (C6′), 111.6 (C4′), 91.5 (C2), 60.2 (OCH_3), 55.6 (OCH_3), 48.5 (C3a), 43.3, 38.6, 26.0, 24.1 and 22.5 ($5CH_2$), 20.8 (CH_3). Remark: carbons hardly relaxed and many signals were weak (notably signals at 120.1, 43.3, 38.6, 26.0, 24.1 and 20.8) or missing (C7a) in all tested solvents ($CDCl_3$, C_6D_6, CD_3OD) at lower or higher temperatures. Anal. calcd for $C_{17}H_{24}N_2O_4$: C, 63.73; H, 7.55; N, 8.74. Found: C, 63.57; H, 7.49, N, 8.68%.

***O*-Methyl-2-propargyl-2-(2,3-dimethoxyphenyl)cyclohexanone-oxime 10.** Ketone **1** (272 mg, 1 mmol) was treated with *O*-methylhydroxylamine hydrochloride (250 mg, 3 mmol) and sodium acetate (246 mg, 3 mmol) in refluxing alcohol (10 mL) for 10 h. This treatment with addition of reagents was renewed three times. The solvent was evaporated and the residue extracted with dichloromethane. Chromatography on silica gel (cyclohexane–methanol 8 : 2) gave **10** (210 mg, 70%) as two isomers. ^{1}H NMR ($CDCl_3$) two isomers. δ 6.9 and 6.8 (2m, ArH), 3.7–3.6 (6s, 3 OCH_3 × 2), 3.1 (m), 3.0–2.7 (m + 2dd, 4H × 2), 1.8 (t, 1H × 2, ≡CH), 1.7–1.2 (m, 6H × 2). ^{13}C NMR ($CDCl_3$) main isomer: δ 163.3 (Cl), 153.4 (C3′), 147.8 (C2′), 134.9 (Cl′), 122.8 (C5′), 121.6 (C6′), 111.2 (C4′), 82.2 (C≡), 70.5 (≡CH), 61.2 (OCH_3), 60.1 (OCH_3), 55.6 (OCH_3), 48.0 (C2), 37.5, 28.9, 27.1, 23.9 and 22.2 (5 CH_2).

7-Methoxy-2-methyl-3a,8a-butano-3a,8a-dihydro-3*H*-benzo-[4,5]furo[2,3-b]pyrrole-1-oxide 11 and its 7-hydroxy analogue 12. Under argon, aluminium trichloride (0.15 g, 11.1 mmol) and methyl sulfide (2 mL) were dissolved at 0 °C in dry dichloromethane (50 mL) and **5** (300 mg, 0.94 mmol), in dry dichloromethane (10mL), was added dropwise; the resulting solution was then allowed to warm up to room temperature. After 20 h stirring, the reaction mixture was diluted with water (5 mL); the organic layer was decanted off, dried and evaporated. The residue was chromatographed on silica gel to give a mixture (230 mg, 76%) of **11** and **12**. The separation of **11** and **12** was accomplished by alkaline washing out.

11: ^{1}H NMR ($CDCl_3$) : δ 6.85 (t, 1H, ArH), 6.7 (2d, 2H, ArH), 3.8 (s, 3H, OCH_3), 2.85 (br s, CH_2–3), 2.7 (br dt, 1H), 2.1–1.1 (m, 7H), 1.95 (br s, CH_3). ^{13}C NMR ($CDCl_3$) : δ145.2 and 144.7 (C7 and C2), 141.9 (C7a), 135.5 (C3b), 123.2 (C5), 114.0 (C4), 112.3 (C6), 110.4 (C8a), 55.9 (OCH_3), 47.7 (C3a), 41.1 (C3), 32.7, 28.6, 19.4 and 18.7 (4 CH_2), 13.0 (CH_3).
Anal. calcd for $C_{16}H_{19}NO_3$: C, 70.05; H 7.35. Found: C, 69.85; H, 7.16%.

12: ^{1}H NMR ($CDCl_3$: δ9.5 (m, OH), 6.9–6.6 (m, 2H, ArH), 6.55 (dd, 1H, ArH), 2.85 (br s, CH_2–3), 2.7 (br dt, 1H), 2.0 (m, 1H), 1.95 (br s, CH_3), 1.9–1.1 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 146.2 (C7), 143.7 and 142.5 (C2 and C7a), 135.0 (C3b), 123.4 (C5), 117.3 (C4), 112.3 (C6), 110.2 (C8a), 48.2 (C3a), 41.2 (C3), 32.8, 28.9, 19.7 and 19.0 (4 CH_2), 13.2 (CH_3). Anal. calcd for $C_{15}H_{17}NO_3$: C, 69.49; H, 6.61. Found: C, 69.79; H, 6.96%.

X-Ray crystallographic data for 12

A total of 2157 reflection data were collected at room temperature with an Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation ($\lambda = 0.7107$ Å; graphite monochromator). Crystal data: $C_{30}H_{34}N_2O_6$, $M_r = 518.59$, triclinic, space group $P\bar{1}$, $a = 7.161(2)$, $b = 8.296(3)$, $c = 11.377(3)$ Å, $\alpha = 77.42(3)$, $\beta = 82.78(3)$, $\gamma = 68.75(3)°$, $V = 613.99$ Å^3, $Z = 2$, $F(000) = 276$, $D_x = 1.403$ M gm^{-3}, white colored block crystal 0.6 × 0.4 × 0.2 mm, μ(Mo-Kα) = 0.10 mm^{-1}. Program used to solve structure: SHELXS-86.[11] Program used to refine the structure: SHELXL93.[12] Non-H atoms were refined with anisotropic displacement parameters and H atoms were refined isotropically. The final value of $R(F)$ is 0.043 for 1479 observed reflections with $I > 2\sigma(I)$ and $wR(F^2) = 0.105$ for all reflections.

CCDC reference number 440/111. See http://www.rsc.org/suppdata/nj/1999/743/ for crystallographic files in .cif format.

Reaction of 13 with hydroxylamine to give 14, 15 and 16

A solution of 2-(propyn-2-yl)cyclohexanone **13** (0.44 g, 3.2 mmol), hydroxylamine hydrochloride (0.45 g, 6.4 mmol) and sodium acetate (0.53 g, 6.4 mmol) in ethyl alcohol (15 mL) was heated under reflux for 18 h. Hydroxylamine hydrochloride (0.23 g, 3.2 mmol and sodium acetate (0.26 g, 3.2 mmol) were added again and the mixture was refluxed for another 24 h. The reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue, purified by chromatography (CH_2Cl_2 then CH_2Cl_2–MeOH 95 : 5) afforded **14** (0.23 g, 47%) and a mixture of **15** and **16** (0.145 g, 25%). Crystallization of this oily mixture in MeOH gave **16** as a slight yellow solid still soiled by **15**.

14: ^{1}H NMR ($CDCl_3$) : δ 9.2 (m, 1H exchangeable), 3.1 (m, 1H), 2.6–1.2 (m, 10H). ^{13}C NMR ($CDCl_3$) : δ 161.0 (C1), 82.7 (C8), 69.6 (C9), 41.4 (C2), 32.5 (C7), 25.9 (C6), 24.5, 24.0 and 20.5 (C3, C4 and C5). Anal. calcd for $C_9H_{13}NO$: C, 71.49; H, 8.66; N, 9.26. Found: C, 71.23; H, 8.52; N, 9.31%.

15: ^{1}H NMR ($CDCl_3$): δ 8.0 (m, 2H exchangeable), 3.8 (m, 0,2H), 2.8–1.0 (m + 2s at 2.1 and 1.9, 14H). ^{13}C NMR ($CDCl_3$), *E* majority isomer: δ 161.6 (C1), 156.8 (C8), 38.7 (C2), 37.1 (C7), 32.0 (C6), 28.5, 25.7 and 23.1 (C3, C4 and C5), 13.6 (C9).

16: ^{1}H NMR (CD_3OD): δ 4.8 (m, 2H exchangeable), 2.7–2.0 (m, 5H), 2.0–1.3 (m + s at 1.83, 9H). ^{13}C NMR (CD_3OD): δ 149.2 (C2), 91.7 (C7a), 39.9 (C3a), 38.0 (C3), 33.2 (C7), 27.0 (C4), 24.0, 23.5 (C5 and C6), 13.4 (CH_38). Anal. calcd for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.20. Found: C, 58.50; H, 8.59; N, 15.14%.

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Paper 9/01896D