Indole and Quinoline Synthesis *via* Intramolecular *Pauson-Khand* Reactions of Enamines and Allylamines

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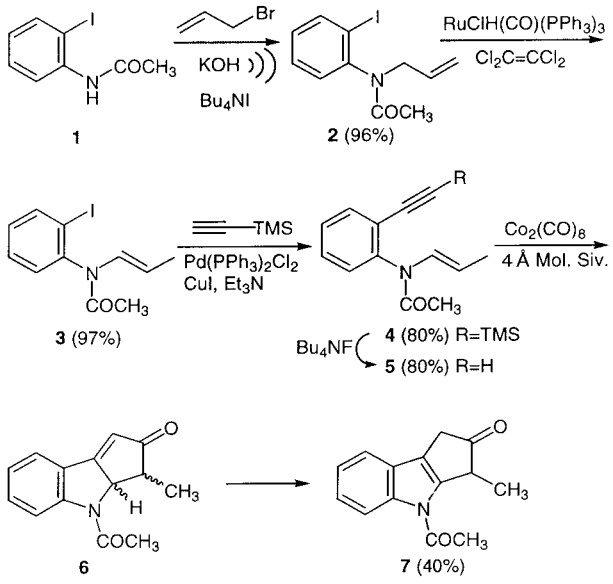
Syntheses of indoles and quinolines based upon the *Pauson-Khand* reaction is described. The starting materials are an aromatic ethynylenamine and ethynylallylamine, which are obtained *via Sonogashira* coupling. Also, an aromatic ynamine is used for an attempt to synthesize indole.

1. Introduction. – The intramolecular *Pauson-Khand* reaction is an important tool for the synthesis of natural products and has been used to obtain many polyheterocyclic systems (for recent reviews, see [1]). Main classical shortcomings of this reaction are low conversions, limited scope, and lack of efficient catalytic versions. A plethora of new promotion methods [2], such as the use of molecular sieves introduced by us [3], have partially solved this problem. Efforts in the field of catalysis have been directed to mild experimental conditions that allow potential applications of this methodology on larger scales (for some recent examples of the catalytic *Pauson-Khand* reaction with Co complexes, see [4]). Also, the general reaction scope continues to widen [5]. In the intermolecular version of this reaction, five- and six-membered rings annulated to the cyclopentenone ring can be obtained with good conversions. The use of enamines as the alkene part of the enyne has not been reported, although alkynylamines have been used for intermolecular *Pauson-Khand* reactions [6]. We have extended the use of the intramolecular *Pauson-Khand* reaction to aromatic benzenic [7] and indolic [8] enynes. With these substrates, we have obtained polycyclic aromatic systems where the *Pauson-Khand* reaction led to the formation of five- to seven-membered [9] rings annulated to the cyclopentenone ring. In this paper, we report the application of the *Pauson-Khand* reaction to aromatic enamines and allylamines to accomplish the synthesis of the indole and quinoline nuclei. We have also tried the reaction of an aromatic alkynylamine to afford an indole.

2. Results. – Allylation at the amidic N-atom of 2-iodoacetanilide **1** with KOH under sonication gave **2** (*Scheme 1*). The *N*-alkenyl amide **3** was obtained *via* isomerization of the C=C bond catalyzed by a Ru complex according to the method of *Krompiec et al.* [10]. The coupling constant for the olefinic H-atoms ($J = 14.6$ Hz) showed the formation of only the (*E*)-isomer. *Sonogashira* coupling [11] with (trimethylsilyl)acetylene gave the corresponding *N*-ynylphenyl *N*-alkenyl amide **4**, which was desilylated to yield **5**. The isomerization of the C=C bond failed, when the *Sonogashira* coupling was performed prior to treatment of the resulting *N*-allyl-*N*-[2-

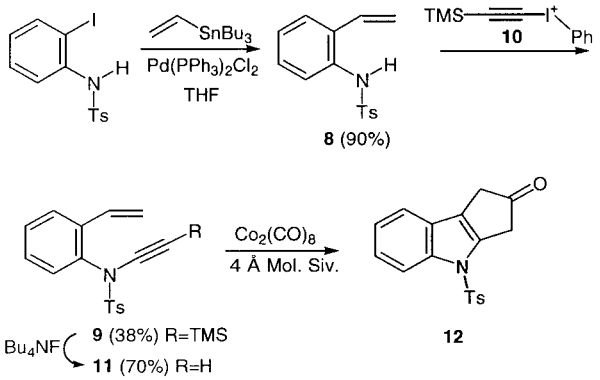
(trimethylsilyl)ethynyl]acetamide with the Ru catalyst. The *Pauson-Khand* reaction was carried out by complexation of **5** with octacarbonyldicobalt at room temperature in toluene, followed by addition of 4-Å molecular sieves and heating. At 70°, the hexacarbonyl cobalt complex did not disappear after 48 h, and the crude mixture showed only a moderate conversion. Upon chromatography, 15% of a 1:1 mixture (calculated from the ^{1}H-NMR spectrum of the crude mixture) of the two diastereoisomers **6** were obtained together with 20% of the desired isomerized indole **7**. To favor the formation of **7**, the reaction temperature was raised to 110°. The result was that the isomers **6** were not detected, and that 40% of the cyclopenta-indole **7** was obtained (*Scheme 1*). The formation of **6** precedes the formation of the more stable **7**, which is favored at higher temperatures (*Scheme 1*). We have described similar isomerizations of other aromatic compounds in *Pauson-Khand* reactions [7].

Scheme 1. *Synthesis of the Cyclopenta-indole* **7**



In another attempt to obtain an cyclopenta-indole nucleus, we carried out the synthesis of *N*-alkynyl-4-methylbenzenesulfonamide **11** starting from *N*-(2-iodophenyl)-4-methylbenzenesulfonamide (*Scheme 2*). *Stille* coupling with tributyl(ethenyl)tin afforded the corresponding *N*-(2-ethenylphenyl) sulfonamide **8**, which reacted with iodonium salt **10** according to the reported procedures [12] to give the *N*-alkynyl **9**, which was desylilated to give **11**. Unfortunately, the *Pauson-Khand* reaction of **11** gave, upon purification, only 15% of the desired cyclopenta-indole **12** together with small amounts of the starting material. We have failed in attempts to isolate this cyclopenta-indole (*Scheme 2*).

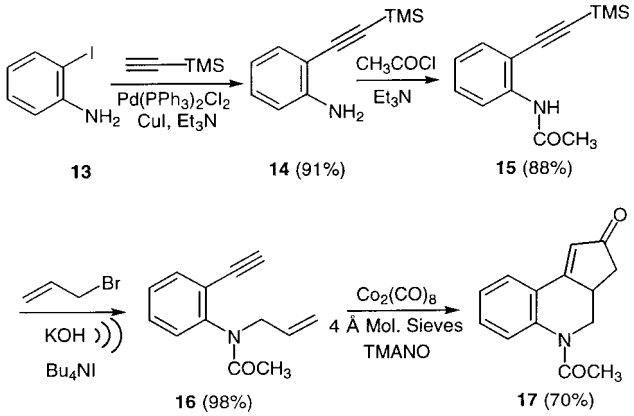
Scheme 2. *Synthesis and* Pauson-Khand *Reaction of* N-*Alkynyl Amide* **11**



The synthesis of the quinolines was accomplished in a similar way starting from 2-iodoaniline (**13**; *Scheme 3*). In this case, best yields were obtained when the *Sonogashira* coupling was performed first to give **14**. This compound was acetylated to give **15**, and the allylation under the same conditions described above gave the *N*-alkenyl *N*-(2-alkynylphenyl) amide **16** after elimination of the Me_3Si (TMS) group. The *Pauson-Khand* reaction of **16** proceeded under milder conditons, and reaction at room temperature with molecular sieves and trimethylamine *N*-oxide (TMANO) gave compound **17** in good yield (70%). When the same experimental procedure as for **7** (molecular sieves in refluxing toluene) was applied, the yield was 65% (*Scheme 3*).

3. Conclusions. – In summary, herein we described the first examples to access the indole nucleus *via* intramolecular *Pauson-Khand* reactions and also to synthesize a quinoline.

Scheme 3. *Synthesis of the Cyclopenta-quinoline* **17**



Experimental Part

General. M.p.: *Büchi 530* apparatus; uncorrected. TLC: *Merck* TLC aluminium sheets (silica gel *60 F_{254}*). Flash column chromatography (FC): *Merck* silica gel (230–400 mesh). IR Spectra: *Perkin-Elmer 1330* spectrophotometer, in cm^{-1}; ^1H- and ^{13}C-NMR spectra: *Bruker AM-300* instrument; chemical shifts are reported as δ values (ppm) downfield from internal Me_4Si in the indicated solvent. Elemental analyses were performed in the *Facultad de Farmacia* (Universidad Complutense Madrid); all anal. values for C, H, and N were within $\pm 0.4\%$ of the theoretical values.

N-*(2-Iodophenyl)*-N-*(prop-2-enyl)acetamide* (**2**). A soln. of 1.6 g (6.1 mmol) of 2-iodoacetanilide and 0.6 ml (6.7 mmol) of allyl bromide in 15 ml of anh. THF was slowly added to a sonicated suspension of 380 mg (6.7 mmol) of KOH and 450 mg (1.22 mmol) of Bu_4NI in 30 ml of dry THF. After 5 h sonication, the crude product was filtered through *Celite*, and the solid washed with Et_2O. The org. phase was washed with H_2O and brine. Evaporation of the solvent and purification by FC (hexane/EtOAc 15%) yielded 1.76 g (96%) of pure **2**. Pale yellow oil. IR (NaCl): 1670. ^1H-NMR ($CDCl_3$): 1.80 (*s*, Me); 3.58 (*dd*, *J* = 14.3, 7.7, 1 H); 4.85 (*dd*, *J* = 14.8, 5.5, 1 H); 5.02–5.12 (*m*, 2 H); 5.84–5.97 (*m*, 1 H); 7.08 (*t*, *J* = 7.7, 1 H); 7.19 (*d*, *J* = 8.2, 1 H); 7.40 (*t*, *J* = 7.7, 1 H); 7.95 (*d*, *J* = 7.7, 1 H). ^{13}C-NMR ($CDCl_3$): 169.3; 144.2; 139.8; 132.3; 130.1; 129.5; 129.1; 118.3; 100.2; 50.6; 22.5.

N-*(2-Iodophenyl)*-N-*(prop-1-enyl)acetamide* (**3**). To a soln. of 4.13 g (13.7 mmol) of **2** in 7.15 ml of $Cl_2C{=}CCl_2$, 135 mg (0.142 mmol) of $[RuClH(CO)(PPh_3)_3]$ were added. The reaction was carried out in air in a pressure tube at 130° for 4.5 h. After this time, the mixture was cooled, filtered through *Celite*, and evaporated to yield 3.97 g (97%) of **3**, which was used without further purification. IR (NaCl): 1670. ^1H-NMR ($CDCl_3$): 1.63 (*dd*, *J* = 6.6, 1.6, 3 H); 1.82 (*s*, 3 H); 4.24–4.35 (*m*, 1 H); 7.13 (*t*, *J* = 7.7, 1 H); 7.26 (*d*, *J* = 7.7, 1 H); 7.37 (*d*, *J* = 14.3, 1 H); 7.48 (*t*, *J* = 7.7, 1 H); 7.97 (*d*, *J* = 7.7, 1 H). ^{13}C-NMR ($CDCl_3$): 167.1; 141.9; 140.0; 129.8; 129.6; 129.4; 126.6; 108.2; 99.8; 22.8; 14.7. Anal. calc. for $C_{11}H_{12}INO$: C 43.87, H 4.02, I 42.14, N 4.65; found: C 43.99, H 4.12, N 4.49.

N-*(Prop-1-enyl)*-N-*{2-[2-(trimethylsilyl)ethynyl]phenyl}acetamide* (**4**). To a soln. of 3.0 g (10.00 mmol) of **3** in 34 ml of dry Et_3N, 1.7 ml (12.00 mmol) of (ethynyl)trimethylsilane, 140 mg (0.20 mmol) of $[Pd(PPh_3)_2Cl_2]$, and 10 mg (0.05 mmol) of CuI were added. The reaction was kept at 70° for 8 h, and the mixture was then cooled, and the solvent was evaporated *in vacuo*. The residue obtained was dissolved in toluene and filtered through *Celite*. The filtrate was concentrated and purified by FC (hexane/AcOEt 95:5): 2.36 g (80%) of pure **4**. Oil. IR (NaCl): 2150, 1670. ^1H-NMR ($CDCl_3$): 0.12 (*s*, 9 H); 1.53 (*d*, *J* = 6.1, 3 H); 1.75 (*s*, 3 H); 4.21–4.32 (*m*, 1 H); 7.10 (*d*, *J* = 7.7, 1 H); 7.25–7.34 (*m*, 3 H); 7.49 (*d*, *J* = 7.1, 1 H). ^{13}C-NMR ($CDCl_3$): 167.7; 141.9; 133.0; 129.6; 129.2; 128.2; 127.8; 123.1; 122.9; 108.2; 100.2; 22.3; 14.8; –0.5. Anal. calc. for $C_{16}H_{21}NOSi$: C 70.80, H 7.80, N 5.16, Si 10.35; found: C 70.95, H 7.89, N 5.01, Si 10.06.

N-*(2-Ethynylphenyl)*-N-*(prop-1-enyl)acetamide* (**5**). To a soln. of 600 mg (2.20 mmol) of **4** in 15 ml of THF at 0°, 4.4 ml (4.40 mmol) of Bu_4NF were added. The mixture was kept at 0° for 30 min. After addition of 25 ml of AcOEt, the soln. was washed with H_2O, dried, and evaporated to give a crude product, which was purified by FC (hexane/AcOEt 85:15): 350 mg (80%) of **5**. IR (NaCl): 3200, 2100, 1660. ^1H-NMR ($CDCl_3$): 1.57 (*dd*, *J* = 7.1, 1.1, 3 H); 1.80 (*s*, 3 H); 3.17 (*s*, 1 H); 4.24–4.36 (*m*, 1 H); 7.16 (*d*, *J* = 7.7, 1 H); 7.32–7.46 (*m*, 3 H); 7.58 (*d*, *J* = 7.7, 1 H). ^{13}C-NMR ($CDCl_3$): 167.9; 141.8; 133.9; 130.1; 129.3; 128.5; 127.9; 122.4; 108.5; 82.1; 78.8; 22.5; 14.9. Anal. calc. for $C_{13}H_{13}NO$: C 78.36, H 6.58, N 7.03; found: C 78.44, H 6.69, N 6.97.

*4-Acetyl-2,3-dihydro-3-methyl-1*H*-cyclopenta[*b*]indol-2-one* (**7**). To a soln. of 130 mg (0.65 mmol) of **5** in 20 ml of anh. toluene, 1.04 g of molecular sieves, and 267 mg (0.78 mmol) of $[Co_2(CO)_8]$ were added. The mixture was stirred under Ar for 2 h at r.t. to allow complexation, and another 15 h under reflux. After cooling, filtration through *Celite*, and concentration, the crude product was purified by FC (hexane/AcOEt 95:5): 60 mg (40%) of pure **7**. White solid. M.p. 141–143° (AcOEt). IR (KBr): 1740, 1700. ^1H-NMR ($CDCl_3$): 1.48 (*d*, *J* = 7.7, 3 H); 2.75 (*s*, 3 H); 3.44 (*s*, 2 H); 3.75 (*q*, *J* = 7.1, 1 H); 7.26–7.39 (*m*, 2 H); 7.48 (*d*, *J* = 7.7, 1 H); 8.01 (*d*, *J* = 8.2, 1 H). ^{13}C-NMR ($CDCl_3$): 216.0; 168.2; 143.0; 137.7; 127.0; 124.7; 123.7; 119.6; 119.5; 115.5; 47.5; 36.8; 25.8; 17.2. Anal. calc. for $C_{14}H_{13}NO_2$: C 73.99, H 5.77, N 6.16; found: C 74.07, H 5.81, N 6.09.

N-*(2-Ethenylphenyl)-4-methylbenzenesulfonamide* (**8**). A suspension of N-*(2-iodophenyl)-4-methylbenzenesulfonamide* (2.80 g, 7.5 mmol) in 20 ml dry THF, 0.27 g (0.4 mmol) $[PdCl_2(PPh_3)_2]$, and 2.68 g (8.47 mmol) of tributyl(vinyl)stannane was refluxed under Ar for 6 h. The mixture was cooled, diluted with Et_2O, and filtered through a pad of neutral alumina. The filtrate was washed several times with H_2O, and the Et_2O phase was dried ($MgSO_4$). Concentration and medium-pressure liquid chromatography (silica gel; hexane/AcOEt 8:2) afforded 1.82 g (90%) of **8**. Yellow solid. M.p. 128–129° (AcOEt). IR (KBr): 3300, 1630, 1600, 1490. ^1H-NMR ($CDCl_3$): 2.39 (*s*, 3 H); 5.26 (*d*, *J* = 14.5, 1 H); 5.50 (*d*, *J* = 17.0, 1 H); 6.52 (*dd*, *J* = 14.5, 17.0, 1 H); 7.11–7.39 (*m*, 1 H, 6 H);

7.60 (*d*, *J* = 8.2, 1 H). ^{13}C-NMR ($CDCl_3$): 143.8; 136.2; 133.0; 132.9; 131.4; 129.5; 128.4; 127.1; 126.7; 126.4; 125.0; 117.8; 21.5. Anal. calc. for $C_{15}H_{15}NO_2S$: C 65.91, H 5.53, N 5.12, S 11.73; found: C 66.05, H 5.51, N 5.08, S 11.65.

N-*(2-Ethenylphenyl)-4-methyl*-N-*[2-(trimethylsilyl)ethynyl]benzenesulfonamide* (**9**). BuLi (1.8 ml of a 1.6M soln. in hexane; 2.9 mmol) was added to a soln. of **8** (0.71 g, 2.6 mmol) in abs. toluene (30 ml) under Ar at 0°. The mixture was allowed to warm to r.t., and then iodonium salt **10** (1.19 g, 2.6 mmol) was added in small portions. The mixture was stirred for 14 h and then filtered through a plug of silica gel and evaporated. The residue was purified by CC (silica gel; hexane/AcOEt 9:1) to give 0.40 g (38%) of **9**. Pale solid. M.p. 106–107° (AcOEt). IR (KBr): 2130, 1590, 1480. ^{1}H-NMR ($CDCl_3$): 0.15 (*s*, 9 H); 2.49 (*s*, 3 H); 5.28 (*d*, *J* = 10.9, 1 H); 5.74 (*d*, *J* = 17.6, 1 H); 6.90 (*m*, 2 H); 7.18 (*t*, *J* = 7.7, 1 H); 7.32–7.38 (*m*, 3 H); 7.64 (*d*, *J* = 7.7, 1 H); 7.69 (*d*, *J* = 8.2, 2 H). ^{13}C-NMR ($CDCl_3$): 145.0; 136.5; 135.6; 133.3; 131.5; 129.4; 129.3; 128.4; 128.3; 128.0; 126.1; 116.2; 95.6; 72.2; 21.6; 0.1. Anal. calc. for $C_{20}H_{23}NO_2SSi$: C 65.00, H 6.27, N 3.79, S 8.68, Si 7.60; found: C 65.24, H 6.40, N 3.68, S 8.49, Si 7.51.

N-*(2-Ethenylphenyl)*-N-*ethynyl-4-methylbenzenesulfonamide* (**11**). A soln. of **9** (0.15 g, 0.4 mmol) in anh. THF (3 ml) was treated with Bu_4NF (0.8 ml of a 1.0M soln. in THF) at 0°. The mixture was stirred at 0° for 45 min, and then it was diluted with hexane/AcOEt (20 ml), washed three times with H_2O (20 ml), dried ($MgSO_4$), and evaporated. The residue was purified by CC (silica gel; hexane/AcOEt 9:1) to give 0.08 g (70%) of **11**. White solid. M.p. 109–110° (AcOEt). IR (KBr): 3280, 2120, 1590, 1480. ^{1}H-NMR ($CDCl_3$): 2.47 (*s*, 3 H); 2.81 (*s*, 1 H); 5.28 (*d*, *J* = 11.0, 1 H); 5.75 (*d*, *J* = 17.6, 1 H); 6.91 (*m*, 2 H); 7.19 (*t*, *J* = 7.7, 1 H); 7.27–7.39 (*m*, 3 H); 7.65 (*d*, *J* = 7.7, 1 H); 7.71 (*d*, *J* = 8.2, 2 H). ^{13}C-NMR ($CDCl_3$): 145.3; 145.4; 136.9; 135.5; 133.8; 131.5; 129.9; 128.7; 128.5; 128.4; 126.5; 116.8; 77.2; 58.3; 21.9. Anal. calc. for $C_{17}H_{15}NO_2S$: C 68.66, H 5.08, N 4.71, S 10.78; found: C 68.80, H 5.20, N 4.63, S 10.57.

Pauson-Khand *Reaction of* **11**. A soln. of $[Co_2(CO)_8]$ (110 mg, 0.31 mmol) in toluene (10 ml) was added to a soln. of **11** (78 mg, 0.26 mmol) in toluene (10 ml) in the presence of molecular sieves (625 mg) under Ar and at r.t. The formation of the carbonylcobalt complex was monitored by TLC (SiO_2; hexane/AcOEt 9:1). After complete formation of the complex, a suspension of trimethylamine *N*-oxide (179 mg, 2.34 mmol) in toluene (10 ml) was added at −10°, and the mixture was allowed to warm to r.t. overnight. The mixture was then filtered through *Celite* and evaporated. The residue was chromatographed on silica gel (elution with hexane/AcOEt 9:1) to give 12 mg of the desired *2,3-dihydro-4-[(4-methylphenyl)sulfonyl]-1*H-*cyclopenta[*b*]indol-2-one* (**12**) together with starting material. ^{1}H-NMR ($CDCl_3$): 2.42 (*s*, 3 H); 3.42 (*s*, 2 H); 3.79 (*s*, 2 H); 7.05–7.47 (*m*, 5 H); 7.95 (*m*, 1 H); 8.01–8.21 (*m*, 2 H).

2-[2-(Trimethylsilyl)ethynyl]aniline (**14**). To a soln. of 1.16 g (5.00 mmol) of 2-iodoaniline (**13**; in 15 ml of dry Et_3N, 0.85 ml (6.00 mmol) of ethynyl(trimethyl)silane, 70 mg (0.10 mmol) of $[Pd(PPh_3)_2Cl_2]$, and 4.8 mg (0.02 mmol) of CuI were added. The reaction was kept at 60° for 5 h and was then cooled to r.t. The solvent was evaporated, and the residue dissolved in toluene and filtered through *Celite*. The filtrate was concentrated and purified by FC (hexane/Et_2O 5%): 0.92 g (91%) of pure **14**. Yellow oil. IR (NaCl): 3480, 3380, 2140. ^{1}H-NMR ($CDCl_3$): 0.24 (*s*, 9 H); 4.20 (br. *s*, 2 H); 6.61–6.67 (*m*, 2 H); 7.09 (*t*, *J* = 7.9, 1 H); 7.26 (*d*, *J* = 7.7, 1 H). ^{13}C-NMR ($CDCl_3$): 148.2; 132.2; 129.8; 117.6; 114.1; 107.7; 101.8; 99.6; 0.1. Anal. calc. for $C_{11}H_{15}NSi$: C 69.78, H 7.99, N 7.40, Si 14.83; found: C 69.85, H 8.07, N 7.33, Si 14.76.

N-*{2-[2-(Trimethylsilyl)ethynyl]phenyl}acetamide* (**15**). A mixture of 1.57 g (8.31 mmol) of **14** in 50 ml of Et_2O and 2.44 ml (17.40 mmol) of Et_3N was cooled to 0° and treated with 1.18 ml (16.50 mmol) of AcCl for 1 h to obtain, after the usual workup, 1.7 g (88%) of pure **15**. Colorless oil. IR (NaCl): 3320, 2140, 1670. ^{1}H-NMR ($CDCl_3$): 0.31 (*s*, 9 H); 2.22 (*s*, 3 H); 7.02 (*t*, *J* = 7.7, 1 H); 7.33 (*t*, *J* = 8.2, 1 H); 7.41 (*d*, *J* = 7.7, 1 H); 8.00 (br. *s*, 1 H); 8.39 (*d*, *J* = 8.2, 1 H). ^{13}C-NMR ($CDCl_3$): 168.0; 139.4; 131.4; 129.9; 123.1; 118.8; 111.4; 102.2; 100.2; 24.8; −0.1. Anal. calc. for $C_{13}H_{17}NOSi$: C 67.49, H 7.41, N 6.05, Si 12.14; found: C 67.77, H 7.60, N 6.01, Si 12.02.

N-*(2-Ethynylphenyl)*-N-*(prop-2-enyl)acetamide* (**16**). A soln. of 1.41 g (6.10 mmol) of **15** and 0.6 ml (6.70 mmol) of allyl bromide in 15 ml of anh. THF was slowly added to a sonicated suspension of 750 mg (13.40 mmol) of KOH and 900 mg (2.44 mmol) of Bu_4NI in 30 ml of dry THF. After 5 h sonication, the crude mixture was filtered through *Celite*, and the solid washed with Et_2O. The org. phase was washed with H_2O and brine. Evaporation of the solvent yielded 1.19 g (98%) of pure **16**. Pale yellow oil. IR (NaCl): 3280, 2100, 1660. ^{1}H-NMR ($CDCl_3$): 1.86 (*s*, 3 H); 3.27 (*s*, 1 H); 3.99 (*dd*, *J* = 14.8, 7.1, 1 H); 4.67 (*dd*, *J* = 14.8, 6.1, 1 H); 5.01–5.09 (*m*, 2 H); 5.87–5.89 (*m*, 1 H); 7.71 (*d*, *J* = 7.7, 1 H); 7.33–7.40 (*m*, 2 H); 7.59 (*d*, *J* = 7.7, 1 H). ^{13}C-NMR ($CDCl_3$): 169.9; 144.2; 133.6; 132.9; 129.7; 129.0; 127.8; 121.8; 117.8; 82.5; 79.4; 51.0; 22.1. Anal. calc. for $C_{13}H_{13}NO$: C 78.36, H 6.58, N 7.03; found: C 78.28, H 6.66, N 7.05.

*5-Acetyl-3,3a,4,5-tetrahydro-2*H-*cyclopenta[c]quinolin-2-one* (**17**). To a soln. of 200 mg (1.00 mmol) of **16** in 30 ml of anh. toluene, 1.60 g of molecular sieves, and 410 mg (1.20 mmol) of $[Co_2(CO)_8]$ were added. After

the mixture was stirred under Ar for 1 h at r.t. to allow complexation, a suspension of 675 mg (9.00 mmol) of trimethylamine *N*-oxide (TMANO) in toluene at $-10°$ was added. Stirring is continued for another 15 h at r.t. Filtration through *Celite* and concentration yield a crude mixture, which was purified by FC (hexane/AcOEt 1:1): 160 mg (70%) of pure **17**. White solid. M.p. 185–187° (AcOEt). IR (KBr): 1690, 1630. ^{1}H-NMR ($CDCl_3$): 2.17 (*dd*, *J* = 18.1, 4.4, 1 H); 2.35 (*s*, 3 H); 2.76 (*dd*, *J* = 17.6, 6.1, 1 H); 3.03 (*t*, *J* = 12.7, 3.14–3.23); (*m*, 1 H); 4.93 (*d*, *J* = 9.3, 1 H); 6.45 (*d*, *J* = 2.2, 1 H); 7.24 (*t*, *J* = 6.6, 1 H); 7.43 (*t*, *J* = 7.2, 1 H); 7.48 (br. *s*, 1 H); 7.73 (*d*, *J* = 7.7, 1 H). ^{13}C-NMR ($CDCl_3$): 205.9; 170.1; 169.9; 139.4; 131.4; 127.2; 125.3; 124.9; 123.9; 122.1; 48.1; 39.5; 39.0; 23.4. Anal. calc. for $C_{14}H_{13}NO_2$: C 73.99, H 5.77, N 6.16; found: C 73.82, H 5.64, N 6.02.

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REFERENCES

[1] T. Sugihara, M. Yamaguchi, M. Nishizawa, *Chem. Eur. J.* **2001**, *7*, 1589; K. M. Brummond, J. L. Kent, *Tetrahedron* **2000**, *56*, 3263; O. Geis, H.-G. Schmalz, *Angew. Chem., Int. Ed*. **1998**, *37*, 911; S. T. Ingate, J. Marco-Contelles, *Org. Prep. Proced. Int*. **1998**, 123.
[2] D. S. Brown, E. Campbell, W. J. Kerr, D. M. Lindsay, A. J. Morrison, K. G. Pike, S. P. Watson, *Synlett* **2000**, 1573; J. G. Ford, W. J. Kerr, G. G. Kirk, D. M. Lindsay, D. Middlemiss, *Synlett* **2000**, 1415; W. J. Kerr, D. M. Lindsay, M. McLaughlin, P. L. Pauson, *Chem. Comm*. **2000**, 1467; T. Sugihara, M. Yamada, M. Yamaguchi, M. Nishizawa, *Synlett* **1999**, 771; B. L. Pagenkopf, T. Livinghouse, *J. Am. Chem. Soc*. **1996**, *118*, 2285; N. Jeong, Y. K. Chung, B. Y. Lee, S. H. Lee, S. E. Yoo, *Synlett* **1991**, 204; V. A. Smit, S. O. Simonyan, V. A. Tarasov, G. S. Mikaelyan, A. S. Gybin, I. I. Ibragimov, R. Caple, D. Froen, A. Kreager, *Synthesis* **1989**, 472; V. A. Smit, S. L. Kireev, O. M. Nefedov, V. A. Tarasov, *Tetrahedron Lett*. **1989**, *30*, 4021.
[3] L. Pérez-Serrano, L. Casarrubios, G. Domínguez, J. Pérez-Castells, *Org. Lett*. **1999**, *1*, 1187.
[4] M. E. Krafft, L. V. R. Bonaga, C. Hirosawa, *J. Org. Chem*. **2001**, *66*, 3004; A. C. Comely, S. E. Gibson, A. Stevenazzi, N. J. Hales, *Tetrahedron Lett*. **2001**, *42*, 1183; T. Rajesh, M. Periasamy, *Tetrahedron Lett*. **1999**, *40*, 817.
[5] J. Wang, M. L. Falck-Pedersen, C. Romming, K. Undheim, *Synth. Commun.* **2001**, *31*, 1141; S. G. Van Ornum, M. M. Bruendl, H. Cao, M. Reddy, D. S. Grubisha, D. W. Bennet, J. M. Cook, *J. Org. Chem*. **2000**, *65*, 1957.
[6] B. Witulski, M. Gossmann, *Synlett* **2000**, 1793; B. Witulski, T. Stengel, *Angew. Chem., Int. Ed*. **1998**, *37*, 489.
[7] L. Pérez-Serrano, J. Blanco-Urgoiti, L. Casarrubios, G. Domínguez, J. Pérez-Castells, *J. Org. Chem*. **2000**, *65*, 3513.
[8] L. Pérez-Serrano, P. González-Pérez, L. Casarrubios, G. Domínguez, J. Pérez-Castells, *Synlett* **2000**, 1303.
[9] L. Pérez-Serrano, L. Casarrubios, G. Domínguez, J. Pérez-Castells, *Chem. Commun*. **2001**, 2602.
[10] S. Krompiec, J. Suwinski, M. Gibas, J. Grobelny, *Pol. J. Chem*. **1996**, *70*, 133.
[11] K. Sonogashira, Y. Tohda, N. Hagihar, *Tetrahedron Lett*. **1975**, *25*, 4467.
[12] M. D. Bachi, N. Bar-Ner, C. M. Crittel, P. J. Stang, B. L. Williamson, *J. Org. Chem*. **1991**, *56*, 3912.

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