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Thermal cyclization of *N*-[2-(2-propenyl)-1-naphthyl] ketenimines: intramolecular Diels–Alder reaction versus [1,5] hydrogen migration. Synthesis of dibenz[*b*,*h*]acridines and benzo[*h*]quinolines

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Dedicated to Professor Joaquín Plumet on the occasion of his 60th birthday

Abstract—The thermal treatment of *N*-(2-propenyl)-1-naphthylamines provided the expected aza-Claisen rearranged products, 2-(2-propenyl)-1-naphthylamines and benz[*g*]indoles, these last derived from an intramolecular hydroamination reaction on those primary products. The 2-(2-propenyl)-1-naphthylamines were converted into their triphenylphosphazene derivatives, which by aza-Wittig reaction with disubstituted ketenes yielded *N*-[2-(2-propenyl)-1-naphthyl] ketenimines. The heating of these ketenimines in boiling toluene induced their cyclization either via an intramolecular Diels–Alder reaction, to afford dibenz[*b*,*h*]acridines, or via [1,5] hydrogen migration from the sp^3 carbon atom of the propenyl substituent to the central carbon atom of the ketenimine fragment, followed by a 6π electrocyclic ring closure, to give benzo[*h*]quinolines.

1. Introduction

The Diels–Alder reaction is undoubtedly one of the most valuable reactions for the synthetic organic chemists due to its widespread utility and enormous synthetic potential.[1] This pericyclic process represents a powerful and effective methodology for the formation of carbon–carbon bonds, which allows high regio and stereoselective constructions of six-membered carbocyclic systems with up to four contiguous new stereogenic centers.[2] This reaction is of particular interest in the total synthesis of naturally occurring products,[3] or structurally related compounds.

The Diels–Alder strategy has likewise found application in the preparation of six-membered heterocyclic compounds by positioning heteroatoms at the diene or at the dienophile (hetero Diels–Alder reaction), and, in its intramolecular version, a heterocycle is also forged by locating a heteroatom in the tether connecting diene and dienophile.[4] On the other hand, the characterization of several natural occurring potential Diels–Alderases established the Diels–Alder reaction as a viable biosynthetic transformation.[5]

In the context of the synthesis of heterocyclic compounds via Diels–Alder reactions, ketenimines [R^1–N=C=CR^2R^3] are valuable precursors for the construction of six-membered heterocycles by means of inter or intramolecular variants of these reactions.[6] These heterocumulenes have the ability to act as 2-azadienes (R^1 = vinyl or aryl group) or as all-carbon dienes (R^2 and/or R^3 = vinyl or aryl group), an even can serve as the dienophile component, with either the N=C or the C=C bond of the ketenimine being involved in the cycloaddition process. As a matter of fact, as part of our research work directed towards the study of the participation of ketenimines in pericyclic processes, we have successfully applied the Diels–Alder strategy to the synthesis of benzo[*d*,*e*][1,6]naphthyridines[7] and pyrido[2,3,4-*d*,*e*]quinazolines[7] (ketenimines as 2-azadienes), benzimidazo[1,2-*b*]isoquinolines[8] and benz[*b*]acridines[9] (ketenimines as all-carbon dienes) and pyrido[1,2-*a*]benzimidazoles[10] (ketenimines as dienophiles by means of its C=C bond).

Our method for preparing benz[*b*]acridines[9] was based on a thermally induced intramolecular Diels–Alder reaction on

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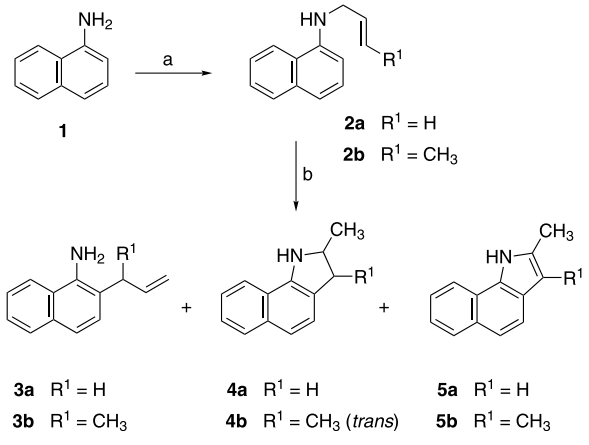
N-[2-(2-propenyl)phenyl]-*C*,*C*-diphenyl ketenimines, in which the ketenimine function acts as an all-carbon diene and the C=C bond of the 2-propenyl side-chain plays the role of the dienophile. With the aim of extending the versatility of this particular methodology we decided to try its application for the synthesis of dibenz[*b*,*h*]acridines,[11] by combination of a *C*-aryl ketenimine fragment (diene) and a 2-propenyl group (dienophile) at the adjacent C1 and C2 carbon atoms of a naphthalene ring. We present herein the results obtained in the thermally induced intramolecular cyclization of *N*-[2-(2-propenyl)-1-naphthyl] ketenimines, forming the expected Diels–Alder adducts, 7,7a,8,14-tetrahydrodibenz[*b*,*h*]acridines, unexpectedly accompanied by benzo[*h*]quinolines, whose formation should involve an initial [1,5] hydrogen migration from the sp^3 carbon atom of the propenyl substituent to the central carbon atom of the ketenimine function.

2. Results and discussion

2.1. Preparation of 2-(2-propenyl)-1-naphthylamines

The *N*-(2-propenyl)-1-naphthylamines **2a**,**b** were both prepared following the reaction conditions reported by Sloviter[12] for the preparation of **2a**, but with a new and simpler protocol that we have developed for the isolation and purification of these two compounds. The reaction of an excess of 1-naphthylamine **1** with 3-chloropropene and 1-chloro-2-butene, in refluxing ethanol for 5 h, yielded only the monoalkylation products **2a** (67% yield) and **2b** (84% yield), respectively. The thermal treatment of neat *N*-(2-propenyl)-1-naphthylamines **2** in a sealed tube at 260–270 °C for 3 h induced their aza-Claisen rearrangement providing 2-(2-propenyl)-l-naphthylamines **3** in approximately 50% yield, whereas a considerable amount (20–30%) of the starting material remained unaltered (Scheme 1). The transformations **2**→**3** were carried out under the reaction conditions described by Marcinkiewicz[12b] and Inada[12c] in their respective preparations of **3a** and **3a**,**b**, but we used a different method in the purification step. We purified the crude materials resulting from these thermal treatments by column chromatography, instead of by distillation or conversion of compounds **3** into their *N*-tosylamines as reported. With the objective of obtaining a total conversion in the transformations **2**→**3** we increased the reaction time. Thus, when the *N*-(2-propenyl) derivative **2a** (R^1=H) was heated at 260–270 °C for 4 h it was totally consumed, and column chromatography of the reaction mixture allowed the isolation of 2-(2-propenyl)-l-naphthylamine **3a** (R^1=H; 38% yield), and, surprisingly, of 2-methyl-2,3-dihydro-1*H*-benz[*g*]indole **4a** (R^1=H; 35% yield) and 2-methyl-1*H*-benz[*g*]indole **5a** (R^1=H; 3% yield) (Scheme 1). A similar thermal treatment of **2b** (R^1=CH_3) for 6 h yielded only *trans*-2,3-dimethyl-2,3-dihydro-1*H*-benz[*g*]indole **4b** (R^1=CH_3; 22% yield) and 2,3-dimethyl-1*H*-benz[*g*]indole **5b** (R^1=CH_3; 21% yield) (Scheme 1).[13]



Scheme 1. Reagents and conditions: (a) CH_2=$CHCH_2Cl$ or CH_3–CH=CH–CH_2Cl, ethanol, reflux, 5 h; (b) 260–270 °C, sealed tube, 3–6 h.

The analytical and spectral data of benz[*g*]indoles **4** and **5** are in accordance with the proposed structures. The *trans* relative positioning of the two methyl groups of **4b** was unequivocally determined by a NOESY experiment. Moreover, the collected data for benzindoles **5** are totally coincident with those previously reported for these compounds.[14]

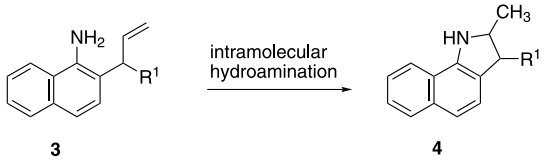
The formation of the 2,3-dihydro-1*H*-benz[*g*]indoles **4** could be explained as occurring by an intramolecular hydroamination reaction of the carbon–carbon double bond of the 2-propenyl substitutent in amines **3** (Scheme 2). Further spontaneous dehydrogenation of **4** under the reaction conditions should give the aromatic derivatives **5**.

The intramolecular hydroamination of aminoalkenes is a well-known reaction, which is usually accomplished by mediation of alkali metals, transition-metals, and actinide and lanthanide complexes.[15] On the other hand, it has been reported that *N*-allylanilines undergo aromatic 3-aza-Cope rearrangement in the presence of HY-Zeolite, HEMT or HZeolite beta, in solution at 80 °C, to afford mixtures of *ortho*-allylanilines and indolines,[16] and in the presence of Zn^{+2} montmorillonite, under microwave irradiation in the absence of solvent, to yield indolines.[17] By contrast, the intramolecular hydroamination occurring in compounds **3** takes place under thermal conditions and in the absence of any catalyst.[18]

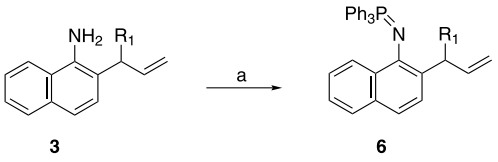
2.2. Thermal cyclization of *N*-[2-(2-propenyl)-1-naphthyl] ketenimines

Triphenylphosphazenes **6** were prepared by reaction of amines **3**, in acetonitrile solution, with triphenylphosphane, carbon tetrachloride and triethylamine (Scheme 3).

Treatment of a toluene solution of triphenylphosphazene **6a** (R^1=H) with diphenylketene at room temperature afforded *N*-[2-(2-propenyl)-1-naphthyl]-*C*,*C*-diphenylketenimine **7a**. The formation of ketenimine **7a** was established by IR spectroscopy: the IR spectrum of the reaction mixture



Scheme 2. Intramolecular hydroamination in the aminoalkenes **3**.

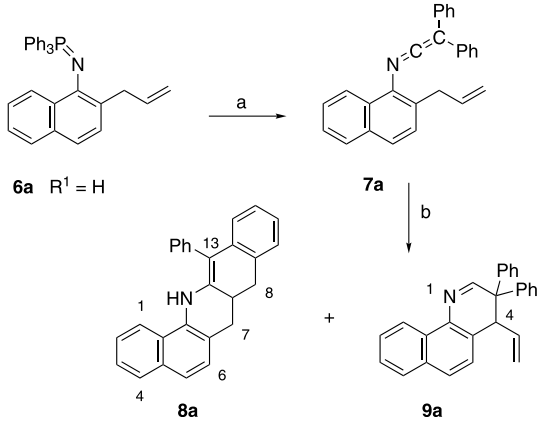


Scheme 3. Reagents and conditions: (a) PPh_3, CCl_4, Et_3N, acetonitrile, rt, 16 h.

showed a strong absorption at 2004 cm^{-1}, characteristic of the N=C=C grouping. Next, the toluene solution containing ketenimine **7a** was heated under reflux up to the total dissapearance of the cumulenic band in its IR spectrum, approximately 1 h. The crude material obtained from this thermal treatment was chromatographed, giving as result the isolation of the expected Diels–Alder cycloadduct 13-phenyl-7,7a,8,14-tetrahydrodibenz[*b*,*h*]acridine (**8a**), in 40% yield, along with a 37% of an unexpected reaction product which was identified as 3,3-diphenyl-4-vinyl-3,4-dihydrobenzo[*h*]quinoline (**9a**) (Scheme 4).

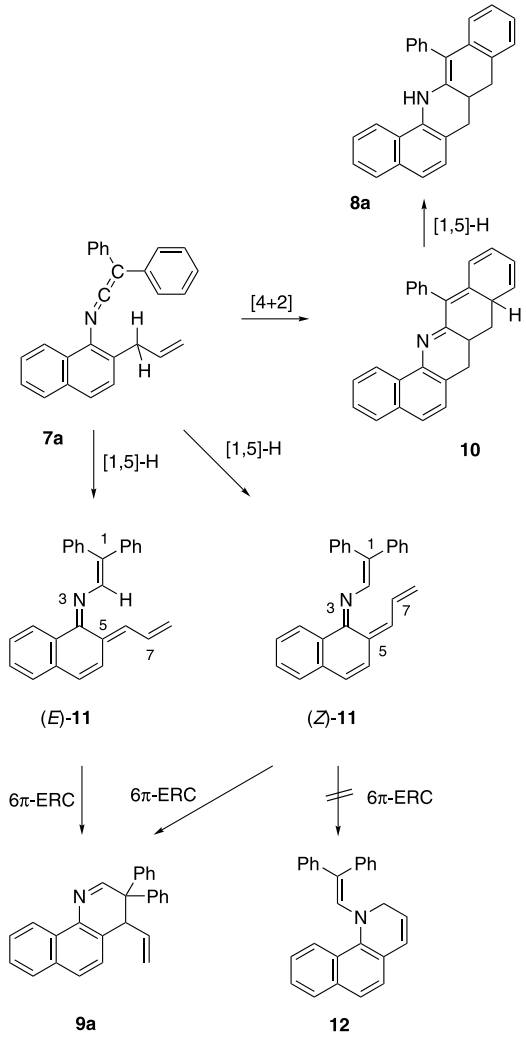
The analytical and spectral data of the dibenz[*b*,*h*]acridine **8a** are essentially similar to those of the benz[*b*]acridines previously prepared by us.[9] The IR spectrum of compound **8a** exhibits a strong absorption at 3428 cm^{-1} due to the vibration of the amino group. In its ^1H NMR spectrum the protons of the two methylene groups appear overlapped in a complex signal at $\delta=2.92$–3.23 ppm. The proton *H*–C7a is observed as a multiplet, at $\delta=3.44$–3.54 ppm. The ^{13}C NMR spectrum of **8a** shows the signals corresponding to the sp^3 hybridized carbon atoms at $\delta=33.4$, 34.9 (C7a) and 36.0 ppm.

In the ^1H NMR spectrum of the benzo[*h*]quinoline **9a** the vinyl substituent is clearly observed, its protons appearing at the following chemical shifts: 4.66 (CH=C$H_A$$H_B$), 4.78 (CH=C$H_A$$H_B$) and 5.54 (C*H*=$CH_2$), all showing the expected multiplicities and coupling constants. In this spectrum, the proton *H*–C2 appears at 8.71 ppm as a doublet, due to a small coupling constant ($^4J=1.2$ Hz, W-type) with *H*–C4, as revealed by a COSY experiment. This last proton appears at $\delta=4.22$ ppm as a broad doublet, as result of its coupling with the vinylic methine proton ($^3J=8.4$ Hz), with the two methylene protons ($^4J=1.0$, 0.6 Hz, allylic-type) and with *H*–C2. The ^{13}C NMR spectrum of compound **9a** shows two signals in the aliphatic region: one at $\delta=49.9$ ppm due to the methine carbon C4, and the other one at $\delta=52.3$ ppm associated to the quaternary carbon atom C3. The methylene carbon of the vinyl group resonates at $\delta=116.9$ ppm, and the signal of the iminic carbon C2 appears at $\delta=164.6$ ppm.



Scheme 4. Reagents and conditions: (a) $Ph_2C=C=O$, toluene, rt, 10 min; (b) Toluene, reflux, 1 h.

The transformation of the *C*,*C*-diphenyl ketenimine **7a** into the tetrahydrodibenz[*b*,*h*]acridine **8a** can be explained by an intramolecular Diels–Alder reaction, the ketenimine fragment acting as all-carbon diene with the participation of its cumulated C=C bond, followed by hydrogen shift. On the other hand, we believe that the conversion of ketenimine **7a** into benzo[*h*]quinoline **9a** takes place by initial [1,5] migration of a hydrogen atom from the benzylic methylene to the central carbon atom of the ketenimine function. This sigmatropic rearrangement may lead to the stereoisomeric intermediates (*E*)-**11** and (*Z*)-**11**, in which the carbon–carbon double bond exocyclic to the naphthalene core is of *E* and *Z* configuration, respectively (Scheme 5). In these intermediates the atoms of the original ketenimine grouping and the 2-propenyl substituent now form part of a conjugated 3-aza-1,3,5,7-octatetraene system. The cyclization of intermediates (*E*)-**11** and (*Z*)-**11** via a 6π electrocyclic ring closure (6π-ERC) involving the

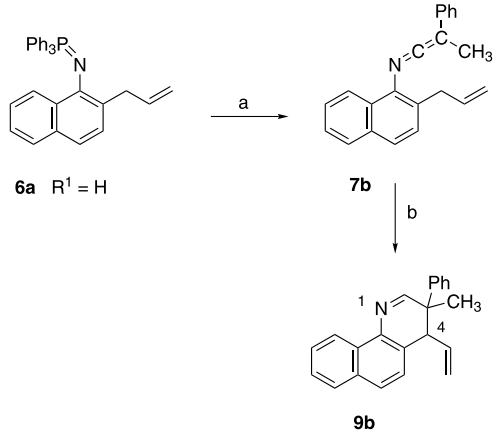


Scheme 5. Proposed mechanism for the conversion **7a**→**8a**+**9a**.

3-azatriene fragment[19] of the 3-aza-1,3,5,7-octatetraene system should provide the 3,4-dihydrobenzo[*h*]quinoline **9a**. Intermediate (*Z*)-**11** has also the appropriate geometry to undergo cyclization by means of an alternative 6π-ERC mode, that involving the 1-azatriene fragment of the 3-aza-1,3,5,7-octatetraene system, affording the benzo[*h*]quinoline **12**. This is not the case, as this compound was not detected in the ^{1}H NMR spectrum of the crude material obtained from the thermal treatment of ketenimine **7a**, before the purification step.

Examples of sigmatropic [1,5]-H shifts to the electrophilic central carbon atom of ketenimines have been occasionally reported. Goerdeler[20] has described that *C*-imidoyl ketenimines underwent, at room temperature, [1,5] hydrogen migration followed by 6π-ERC to yield dihydropyrimidines, whereas Foucaud[21] has demonstrated that, in refluxing dichloromethane, *N*-imidoyl ketenimines converted into pyrrolotriazines by [1,5]-H shift followed by intramolecular [4+2] cycloaddition. More recently, Wentrup[22] has reported that *N*-phenyl ketenimines bearing methyl groups at the *ortho* position to the nitrogen atom, under very mild flash vacuum thermolysis conditions (350 °C), suffer a facile [1,5] hydrogen migration and subsequent electrocyclization to dihydroquinolines.

The generation of *N*-[2-(2-propenyl)-1-naphthyl] ketenimines bearing one or two alkyl substituent at the terminal carbon atom of the ketenimine moiety instead of phenyl groups should, respectively, decrease or prevent the probability of occurring the [4+2] cyclization mode. Thus the evolution of such ketenimines via the sequence [1,5]-H/6π-ERC should be favoured. A major limitation that we found in the preparation of ketenimines by the aza-Wittig reaction of phosphazenes with ketenes is that only ketenes that are stable enough to be isolated under usual working conditions could be employed successfully.[23] Thus, we carried out the reaction of triphenylphosphazene **6a** (R^1=H), in toluene solution at room temperature, with the isolable methylphenylketene to generate the *C*-methyl-*C*-phenyl ketenimine **7b** (Scheme 6). When this ketenimine was heated in refluxing toluene it experienced cyclization to 3-methyl-3-phenyl-4-vinyl-3,4-dihydrobenzo[*h*]quinoline (**9b**), which was obtained as a 1:1 mixture of *cis* and *trans* diastereoisomers in good yield (73%).

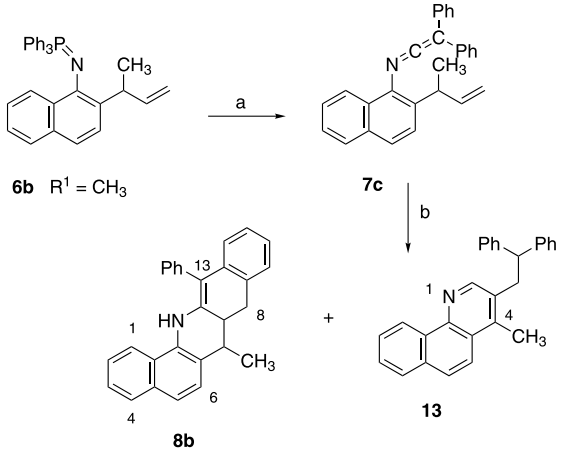


Scheme 6. Reagents and conditions: (a) $Ph(CH_3)C{=}C{=}O$, toluene, rt, 10 min; (b) Toluene, reflux, 1 h.

This result suggests that in *N*-[2-(2-propenyl)-1-naphthyl] ketenimines **7** the presence of one alkyl substituent at their terminal carbon atom is enough to bring about their cyclization periselectively via the consecutive [1,5] hydrogen migration/6π electrocyclic ring closure path.

Expecting a similar chemical behavior to that observed for the *C*,*C*-diphenyl ketenimine **7a** we prepared the methyl substituted analogue **7c** (Scheme 7), although it emerged not to be the case. The difference between these two ketenimines is the presence in **7c** of a methyl group at the sp^3 carbon atom of the side chain. Two different fractions were collected when the crude material that resulted from the heating of ketenimine **7c** in toluene at reflux temperature for 1 h was chromatographed. The first one consisted on a 1:1 mixture of the two possible diastereoisomers of 7-methyl-13-phenyl-7,7a,8,14-tetrahydrodibenz[*b*,*h*]acridine (**8b**), along with a small amount of an unidentified impurity we were not able to separate chromatographically. Compound **8b** was separated from the impurity by crystallization from diethyl ether. This is the reason why pure **8b** was obtained in low yield (14%). The crystalline product still consisted on both diastereoisomers of **8b** in a 1:1 ratio. From the second chromatographic fraction 3-(2,2-diphenylethyl)-4-methylbenzo[*h*]quinoline (**13**) was isolated in 17% yield.

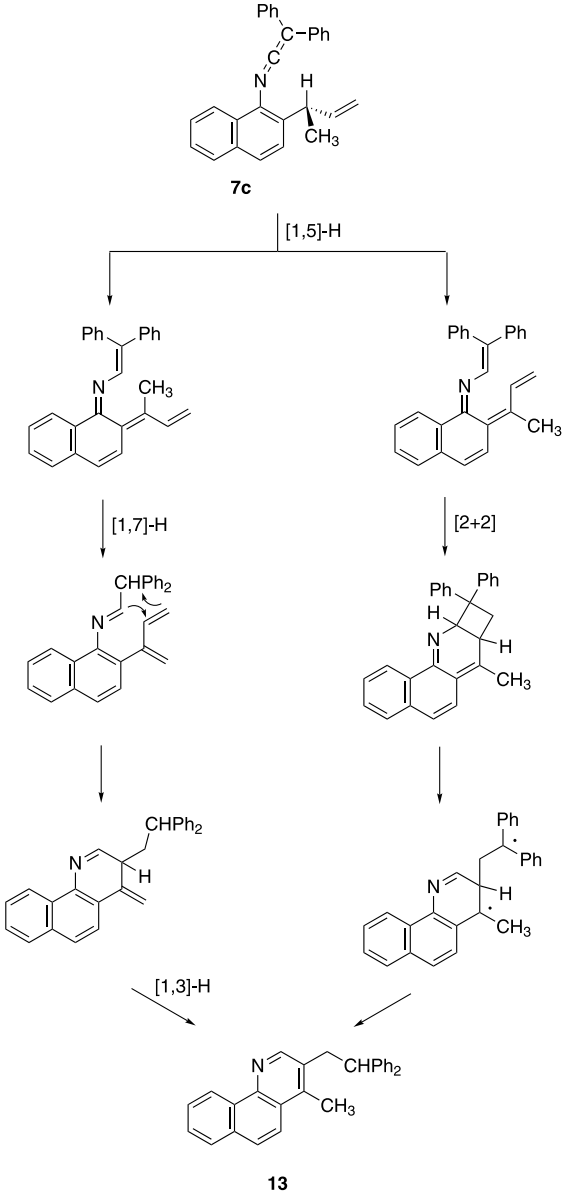
The structures of compounds **8b** and **13** were confirmed by their analytical and spectroscopic data. The main features of the ^{1}H NMR spectrum of benzo[*h*]quinoline **13** are the following: a singlet at δ=2.46 ppm, associated with the methyl group C*H*$_3$–C4, a doublet and a triplet at δ=3.61 ppm and δ=4.27 ppm, respectively, assigned to the methylene and methine protons of the diphenylethyl substituent at C3, and a singlet at δ=8.49 ppm attributed to the proton *H*–C2. The positions of the diphenylethyl and methyl substituents at the benzoquinoline ring were determined by performing NOESY and NOE difference experiments. These experiments associated the signals of the diphenylethyl group with those of *H*–C2 and C*H*$_3$–C4. *H*–C2 and C*H*$_3$–C4, in turn, did not show any effect on each other. Also NOE effect was observed between *H*–C5 and the methyl group.



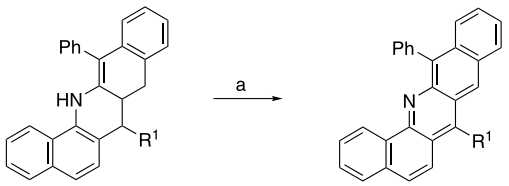
Scheme 7. Reagents and conditions: (a) $Ph_2C{=}C{=}O$, toluene, rt, 10 min; (b) Toluene, reflux, 1 h.

The formation of the dibenzacridine **8b** is easily understood as occurring by an intramolecular Diels–Alder reaction in ketenimine **7c**, whereas the formation of benzoquinoline **13** should occur by a new, more complex, mechanistic pathway. Probably, the conversion **7c**→**13** is initiated by an [1,5] hydrogen migration from the sp^3 carbon of the propenyl substituent to the central carbon of the ketenimine function, as it could be ascertained by the presence of an hydrogen atom at carbon 2 of compound **13**. After this first hydrogen shift the resulting intermediate could undergo evolution to the benzoquinoline **13**, for example, either by means of a sequence of shifts or by a mechanistic pathway involving the formation of birradical species, as it is shown in Scheme 8.

The aza-Wittig reaction of triphenylphosphazene **6b** with methylphenylketene, and the subsequent thermal treatment of the resulting *C*-methyl-*C*-phenyl ketenimine only gave, in our hands, very complex reaction mixtures.



Scheme 8. Two mechanistic proposals for explaining the conversion of **7c** into **13**.



Scheme 9. Reagents and conditions: (a) Pd/C, *ortho*-xylene, reflux, 3 h.

2.3. Preparation of aromatic dibenz[*b*,*h*]acridines

Finally, the 7,7a,8,14-tetrahydrodibenz[*b*,*h*]acridines **8** could be easily oxidized in refluxing *ortho*-xylene in the presence of Pd/C to give the fully aromatic dibenz[*b*,*h*]-acridines **14** (Scheme 9). Compounds **14** were thus obtained in almost quantitative yields (82–97%).

3. Conclusion

In summary, in this work we have reported that under thermal conditions, and in the absence of any catalyst, 2-(2-propenyl)-1-naphthylamines undergo a formal intramolecular hydroamination reaction to yield 2,3-dihydrobenz[*g*]indoles. We have also described how *N*-[2-(2-propenyl)-1-naphthyl] ketenimines undergo cyclization either by a Diels–Alder cycloaddition or by an [1,5] hydrogen migration followed by a 6π electrocyclic ring closure, providing new routes to dibenz[*b*,*h*]acridines and benzo[*h*]quinolines. The mode selectivity, Diels–Alder cycloaddition versus [1,5] hydrogen migration, found in the cyclization of the *N*-[2-(2-propenyl)-1-naphthyl] ketenimines prepared depends basically on the nature of the substituents at the terminal carbon atom of the ketenimine function.

4. Experimental

4.1. General method

All mps were determined on a Kofler hot-plate mp apparatus and are uncorrected. IR spectra were obtained as films or Nujol emulsions on a Nicolet Impact 400 spectrophotometer. NMR spectra were recorded on a Bruker Avance 300 (300, 75 MHz for ^1H and ^{13}C, respectively) or a Bruker Avance 400 (400 and 100 MHz for ^1H and ^{13}C, respectively), in $CDCl_3$ as solvent, and the chemical shifts are expressed in ppm relative to Me_4Si at $\delta=0.00$ for ^1H and to $CDCl_3$ at $\delta=77.1$ for ^{13}C. Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer or on a VG-Autospec spectrometer. Microanalyses were performed on a Carlo Erba EA-1108 instrument.

4.2. Materials

Diphenylketene[24] and methylphenylketene[25] were prepared according to literature procedures.

4.3. General procedure for the preparation of *N*-(2-propenyl)-1-naphthylamines 2

1-Naphthylamine **1** (12.88 g, 90 mmol) was dissolved in ethanol (100 ml) and 3-chloropropene (2.29 g, 30 mmol) or 1-chloro-2-butene (2.71 g, 30 mmol) was added. The reaction mixture was heated at reflux temperature for 5 h. After cooling at room temperature, the solvent was removed under reduced pressure, and aqueous NaOH 5% (200 ml) was added to the solid residue. The resulting suspension was stirred at room temperature for 5 min, and then extracted with dichlorometane (2×75 ml). The combined organic layer was washed with water (100 ml) and dried over anhydrous $MgSO_4$. The dichloromethane was removed under reduced pressure and the resulting material was purified by column chromatography [silica gel; hexanes/diethyl ether 9:1 (v/v)].

4.3.1. *N*-(2-Propenyl)-1-naphthylamine[12a] (2a). Yield 67%. ^{1}H NMR ($CDCl_3$) δ=3.92 (d, 2H, J=5.2 Hz), 4.43 (br s, 1H), 5.18–5.24 (m, 1H), 5.29–5.40 (m, 1H), 5.96–6.16 (m, 1H), 6.65 (d, 1H, J=7.4 Hz), 7.20–7.44 (m, 4H), 7.75–7.81 (m, 2H).

4.3.2. (*E*)-*N*-(2-Butenyl)-1-naphthylamine[12e] (2b). Yield 84%. ^{1}H NMR ($CDCl_3$) δ=1.78–1.83 (m, 3H), 3.88–3.90 (m, 2H), 4.38 (br s, 1H), 5.73–5.91 (m, 2H), 6.67 (dd, 1H, J=7.5, 0.9 Hz), 7.28–7.31 (m, 1H), 7.37–7.52 (m, 3H), 7.81–7.86 (m, 2H).

4.4. Thermal treatment of *N*-(2-propenyl)-1-naphthylamine 2a

N-(2-Propenyl)-1-naphthylamine **2a** (3.66 g, 20 mmol) was heated in a sealed tube at 260–270 °C for 4 h. After cooling at room temperature, the crude material was dissolved in dichloromethane (20 ml) and transferred to a round bottom flask. The solvent was removed under reduced pressure and the resulting oil was chromatographed on a silica gel column using hexanes/diethyl ether (4:1, v/v) as eluent. The fractions containing the major component were combined and the solvent removed under reduced pressure to give an oily residue which was subjected to a second column chromatography using dichloromethane/hexanes (9:1; v/v) as eluent.

4.4.1. 2-(2-Propenyl)-1-naphthylamine[12b] (3a). Yield 38%. ^{1}H NMR ($CDCl_3$) δ=3.47 (dt, 2H, J=6.2, 1.7 Hz), 4.16 (br s, 2H), 5.09 (dq, 1H, J=8.2, 1.7 Hz), 5.14–5.56 (m, 1H), 5.90–6.10 (m, 1H), 7.20 (d, 1H, J=8.4 Hz), 7.29 (d, 1H, J=8.4 Hz), 7.36–7.48 (m, 2H), 7.73–7.83 (m, 2H).

4.4.2. 2-Methyl-2,3-dihydro-1*H*-benz[*g*]indole (4a). Yield 35%; mp 76–77 °C; colorless prisms (*n*-hexane). ^{1}H NMR ($CDCl_3$) δ=1.34 (d, 3H, J=6.3 Hz), 2.81 (dd, 1H, J=15.3, 7.5 Hz), 3.32 (dd, 1H, J=15.3, 9.0 Hz), 3.89 (br s, 1H), 4.10–4.18 (m, 1H), 7.26 (s, 2H), 7.31–7.38 (m, 2H), 7.55–7.59 (m, 1H), 7.74–7.79 (m, 1H). ^{13}C NMR ($CDCl_3$) δ= 22.7, 38.6, 55.7, 118.7, 120.7 (s), 121.4, 122.5 (s), 123.6, 124.7, 125.0, 128.5, 133.5 (s), 146.3 (s). MS *m*/*z* (I%): 183 (M^+, 63), 168 (100). IR (nujol) ν cm^{-1}: 3355, 1575, 1523, 1423, 1332, 1284, 1160, 1126, 1103, 1080, 880, 867, 803, 767, 749, 674. Anal. Calcd for $C_{13}H_{13}N$: C, 85.20; H, 7.15; N, 7.65. Found: C, 85.03; H, 7.18; N, 7.77.

4.4.3. 2-Methyl-1*H*-benz[*g*]indole[14a] (5a). Yield 3%. ^{1}H NMR ($CDCl_3$) δ=2.45 (d, 3H, J=0.9 Hz), 6.32–6.34 (m, 1H), 7.36 (ddd, 1H, J=8.1, 6.9, 1.3 Hz), 7.41–7.48 (m, 2H), 7.61 (dd, 1H, J=8.6, 0.3 Hz), 7.80–7.83 (m, 1H), 7.86–7.89 (m, 1H), 8.45 (br s, 1H).

4.5. Thermal treatment of (*E*)-*N*-(2-butenyl)-1-naphthylamine 2b

(*E*)-*N*-(2-Butenyl)-1-naphthylamine **2b** (3.94 g, 20 mmol) was heated in a sealed tube at 260–270 °C for 3 h. After cooling at room temperature, the crude material was dissolved in dichloromethane (20 ml) and transferred to a round bottom flask. The solvent was removed under reduced pressure and the resulting oil was chromatographed on a silica gel column using dichloromethane/hexanes (4:1, v/v) as eluent.

In this reaction a 25% of the starting material was recovered.

4.5.1. 2-(1-Methyl-2-propenyl)-1-naphthylamine[12c] (3b) Yield 54%. ^{1}H NMR ($CDCl_3$) δ=1.48 (d, 3H, J=7.0 Hz), 3.64–3.72 (m, 1H), 4.24 (br s, 2H), 5.11 (dt, 1H, J=6.2, 1.6 Hz), 5.14–5.15 (m, 1H), 5.99–6.07 (m, 1H), 7.28 (d, 1H, J=8.5 Hz), 7.32 (d, 1H, J=8.5 Hz), 7.38–7.46 (m, 2H), 7.75–7.81 (m, 2H).

When (*E*)-*N*-(2-butenyl)-1-naphthylamine **2b** was heated at 260–270 °C for 6 h the reaction products were *trans*-2,3-dimethyl-2,3-dihydro-1*H*-benz[*g*]indole **4b** and 2,3-dimethyl-1*H*-benz[*g*]indole **5b**.

4.5.2. *trans*-2,3-Dimethyl-2,3-dihydro-1*H*-benz[*g*]indole (4b). Yield 22%; dark oil. ^{1}H NMR ($CDCl_3$) δ=1.37 (d, 3H, J=6.8 Hz), 1.41 (d, 3H, J=6.2 Hz), 3.04 (dq, 1H, J= 8.7, 6.8 Hz), 3.64 (dq, 1H, J=8.7, 6.2 Hz), 3.74 (br s, 1H), 7.23–7.31 (m, 2H), 7.35–7.45 (m, 2H), 7.60–7.63 (m, 1H), 7.75–7.81 (m, 1H). ^{13}C NMR ($CDCl_3$) δ=18.3, 21.1, 45.2, 64.5, 118.9, 120.7 (s), 121.5, 122.2, 124.7, 125.1, 127.9 (s), 128.5, 133.6 (s), 145.6 (s). MS *m*/*z* (I%): 197 (M^+, 27), 194 (100). IR (nujol) ν cm^{-1}: 3368, 1574, 1519, 1453, 1441, 1420, 1375, 1335, 1267, 1257, 1082, 976, 937, 805, 777, 747, 678. Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.05; H, 7.78; N, 7.16.

4.5.3. 2,3-Dimethyl-1*H*-benz[*g*]indole[14d] (5b). Yield 21%. ^{1}H NMR ($CDCl_3$) δ=2.28 (d, 3H, J=0.5 Hz), 2.40 (s, 3H), 7.35 (ddd, 1H, J=8.2, 6.9, 1.2 Hz), 7.45 (ddd, 1H, J=8.2, 6.9, 1.2 Hz), 7.47 (d, 1H, J=8.2 Hz), 7.59 (d, 1H, J= 8.6 Hz), 7.87 (t, 2H, J=8.9 Hz), 8.32 (br s, 1H).

4.6. General procedure for the preparation of 2-(2-propenyl)-1-(triphenylphosphoranylideneamino) naphthalenes 6

The corresponding 2-(2-propenyl)-1-naphthylamine **3** (10 mmol) and triphenylphosphane (5.24 g, 20 mmol) were dissolved in a mixture of anhydrous acetonitrile (25 ml) and triethylamine (15 ml). Then carbon tetrachloride was added (10 ml), and the reaction mixture was kept at

room temperature without stirring for 16 h. The precipitated solid was filtered and washed with anhydrous acetonitrile (2×2 ml). From the filtrate the solvent was removed under reduced pressure, and the crude material was purified by column chromatography using silica gel deactivated with triethylamine as solid phase and hexanes/diethyl ether (3:2, v/v) as eluent. After removing the solvent from the combined fractions containing **6** the resulting white solid was treated with diethyl ether (5 ml), filtered and dried.

4.6.1. 2-(2-Propenyl)-1-(triphenylphosphoranylideneamino)naphthalene (6a). Yield 49%; mp 131–132 °C; colorless prisms (diethyl ether/*n*-pentane). ^{1}H NMR ($CDCl_3$) δ=3.32 (ddd, 2H, J=6.5, 3.1, 1.5 Hz), 4.78–4.86 (m, 2H), 5.59–5.69 (m, 1H), 6.97 (ddd, 1H, J=8.1, 6.8, 1.0 Hz), 7.17–7.22 (m, 2H), 7.25 (dd, 1H, J=8.3, 2.5 Hz), 7.35–7.40 (m, 6H), 7.45–7.50 (m, 3H), 7.58–7.65 (m, 7H), 7.99 (d, 1H, J=8.3 Hz). ^{13}C NMR ($CDCl_3$) δ=37.1 (d, J=1.3 Hz), 114.7, 118.9 (d, J=3.6 Hz), 123.6, 124.2, 126.0, 127.5, 128.3 (d, J=3.3 Hz), 128.5 (d, J=12.2 Hz), 129.0 (d, J=8.7 Hz) (s), 131.4 (d, J=2.6 Hz), 132.2 (d, J=5.7 Hz) (s), 132.4 (d, J=101.3 Hz) (s), 132.6 (d, J=9.6 Hz), 133.8 (d, J=2.1 Hz) (s), 138.4 (d, J=1.2 Hz), 143.9 (d, J=1.6 Hz) (s). ^{31}P NMR ($CDCl_3$, 121 MHz, H_3PO_4) δ=−2.4. MS *m*/*z* (I%): 443 (M^+, 5), 262 (100). IR (nujol) ν cm^{-1}: 1637, 1557, 1407, 1153, 1131, 1116, 996, 843, 808, 755, 747, 725, 713, 696. Anal. Calcd for $C_{31}H_{26}NP$: C, 83.95; H, 5.91; N, 3.16. Found: C, 83.79; H, 5.78; N, 3.10.

4.6.2. 2-(1-Methyl-2-propenyl)-1-(triphenylphosphoranylideneamino)naphthalene (6b). Yield 42%; mp 138–139 °C; colorless prisms (diethyl ether/*n*-pentane). ^{1}H NMR ($CDCl_3$) δ=0.98 (d, 3H, J=7.0 Hz), 4.05–4.12 (m, 1H), 4.77 (dt, 1H, J=17.3, 1.9 Hz), 4.83 (dt, 1H, J=10.5, 1.9 Hz), 5.57 (ddd, 1H, J=17.3, 10.5, 4.9 Hz), 6.97 (ddd, 1H, J=8.2, 6.8, 1.1 Hz), 7.14 (dd, 1H, J=8.5, 1.5 Hz), 7.20 (ddd, 1H, J=8.0, 6.8, 1.1 Hz), 7.28 (dd, 1H, J=8.5, 2.5 Hz), 7.36–7.41 (m, 6H), 7.47–7.51 (m, 3H), 7.57–7.65 (m, 7H), 8.00 (d, 1H, J=8.5 Hz). ^{13}C NMR ($CDCl_3$) δ=19.3, 37.0, 111.8, 119.2 (d, J=3.8 Hz), 123.7, 124.3, 126.0 (d, J=3.1 Hz), 126.3 (d, J=1.3 Hz), 127.5, 128.5 (d, J=11.9 Hz), 131.4 (d, J=2.8 Hz), 132.2 (d, J=5.5 Hz) (s), 132.3 (d, J=101.2 Hz) (s), 132.6 (d, J=9.5 Hz), 133.6 (d, J=2.2 Hz) (s), 134.2 (d, J=8.8 Hz) (s), 143.2 (d, J=2.8 Hz) (s), 143.8 (d, J=1.1 Hz). ^{31}P NMR ($CDCl_3$, 121 MHz, H_3PO_4) δ=−2.0. MS *m*/*z* (I%): 457 (M^+, 17), 262 (100). IR (nujol) ν cm^{-1}: 1630, 1559, 1505, 1436, 1303, 1158, 1131, 1114, 1098, 1029, 997, 897, 749, 727, 713, 697. Anal. Calcd for $C_{32}H_{28}NP$: C, 84.00; H, 6.17; N, 3.06. Found: C, 84.19; H, 6.06; N, 3.10.

4.7. Reaction of 2-(2-propenyl)-1-(triphenylphosphoranylideneamino)naphthalene 6a with ketenes

To a solution of 2-(2-propenyl)-1-(triphenylphosphoranylideneamino)naphthalene **6a** (0.55 g, 1.25 mmol) in anhydrous toluene (20 ml) a solution of diphenylketene (0.34 g, 1.75 mmol) or methylphenylketene (0.23 g, 1.75 mmol) in the same solvent (5 ml) was added. The reaction mixture was stirred at room temperature for 10 min, and then heated at reflux temperature for 1 h. After cooling at room temperature, the solvent was removed under reduced pressure and the crude material was chromatographed on a silica gel column using hexanes/diethyl ether (9:1, v/v) as eluent.

4.7.1. 13-Phenyl-7,7a,8,14-tetrahydrodibenz[*b*,*h*]acridine (8a). Yield 40%; mp 212–213 °C; yellow prisms (diethyl ether). ^{1}H NMR ($CDCl_3$) δ=2.92–3.13 (m, 4H), 3.44–3.54 (m, 1H), 6.52 (dd, 1H, J=7.6, 1.2 Hz), 6.79 (s, 1H), 6.91 (td, 1H, J=7.2, 1.4 Hz), 6.95–6.99 (m, 1H), 7.07 (d, 2H, J=8.3 Hz), 7.13 (d, 1H, J=8.3 Hz), 7.21 (d, 1H, J=8.3 Hz), 7.26–7.34 (m, 2H), 7.40–7.42 (m, 2H), 7.46 (tt, 1H, J=7.4, 1.4 Hz), 7.56–7.60 m, 2H), 7.68–7.71 (m, 1H). ^{13}C NMR ($CDCl_3$) δ=33.4, 34.9, 36.0, 110.1 (s), 116.4 (s), 118.3, 118.8, 121.5 (s), 122.9, 123.7, 125.2, 125.4, 126.7, 126.8, 126.9, 127.7, 128.8, 129.8, 131.2, 131.6 (s), 133.5 (s), 133.7 (s), 137.0 (s), 138.1 (s), 138.2 (s). MS *m*/*z* (I%): 359 (M^+, 76), 354 (100). IR (nujol) ν cm^{-1}: 3428, 1622, 1594, 1563, 1334, 1314, 1293, 1277, 1182, 1156, 1098, 1011, 857, 803, 759, 737. Anal. Calcd for $C_{27}H_{21}N$: C, 90.21; H, 5.89; N, 3.90. Found: C, 90.35; H, 5.78; N, 3.83.

4.7.2. 3,3-Diphenyl-4-vinyl-3,4-dihydrobenzo[*h*]quinoline (9a). Yield 37%; mp 151–152 °C; colorless prisms (diethyl ether/*n*-pentane). ^{1}H NMR ($CDCl_3$) δ=4.22 (d, 1H, J=8.4 Hz), 4.66 (ddd, 1H, J=16.9, 1.5, 1.0 Hz), 4.78 (ddd, 1H, J=10.1, 1.5, 0.6 Hz), 5.54 (ddd, 1H, J=16.9, 10.1, 8.4 Hz), 7.08–7.16 (m, 3H), 7.19–7.33 (m, 7H), 7.36 (d, 1H, J=8.3 Hz), 7.40–7.53 (m, 2H), 7.77 (d, 2H, J=8.3 Hz), 8.56–8.60 (m, 1H), 8.71 (d, 1H, J=1.2 Hz). ^{13}C NMR ($CDCl_3$) δ=49.9, 52.3 (s), 116.9, 123.6, 124.9 (s), 125.9, 126.0, 126.5, 126.9, 127.0, 127.7, 128.2, 128.3, 128.4, 128.6, 128.8, 130.3 (s), 133.5 (s), 136.1, 136.3 (s), 142.9 (s), 143.8 (s), 164.6. MS *m*/*z* (I%): 359 (M^+, 93), 165 (100). IR (nujol) ν cm^{-1}: 1617, 1596, 1497, 1185, 1149, 1128, 1037, 997, 971, 951, 925, 885, 823, 768, 752, 701. Anal. Calcd for $C_{27}H_{21}N$: C, 90.21; H, 5.89; N, 3.90. Found: C, 90.32; H, 5.80; N, 3.79.

4.7.3. 3-Methyl-3-phenyl-4-vinyl-3,4-dihydrobenzo[*h*]quinoline (9b). Yield 73%. Mixture of two diastereoisomers (1:1). ^{1}H NMR ($CDCl_3$) δ=1.49 (s, 3H), 1.59 (s, 3H), 3.57 (d, 1H, J=8.9 Hz), 3.77 (d, 1H, J=9.4 Hz), 4.88–5.12 (m, 4H), 5.36–5.45 (m, 1H), 5.81–5.90 (m, 1H), 7.16–7.32 (m, 12H), 7.44–7.82 (m, 8H), 8.07 (s, 1H), 8.21 (s, 1H), 8.70 (d, 1H, J=8.4 Hz), 8.76 (d, 1H, J=8.4 Hz). ^{13}C NMR ($CDCl_3$) δ=19.5, 23.2, 43.7 (s), 43.8 (s), 52.5, 52.6, 118.2, 118.7, 123.6, 123.7, 124.3 (s), 124.6 (s), 125.7, 125.8, 125.9, 126.0, 126.4, 126.5, 126.7, 126.8, 127.1, 127.5, 127.6, 127.7, 127.9, 128.4, 128.5, 130.1 (s), 130.2 (s), 133.2 (s), 133.5 (s), 133.6 (s), 135.0, 136.3, 136.7 (s), 140.0 (s), 144.0 (s), 167.8, 168.4. MS *m*/*z* (I%): 297 (M^+, 66), 280 (100). IR (neat) ν cm^{-1}: 1620, 1600, 1582, 1562, 1494, 1444, 1376, 1264, 1212, 1144, 1074, 1028, 1000, 922, 818, 758. Anal. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.55; H, 6.78; N, 4.66.

4.8. Reaction of 2-(1-methyl-2-propenyl)-1-(triphenylphosphoranylideneamino)naphthalene 6b with diphenylketene

To a solution of 2-(1-methyl-2-propenyl)-1-(triphenylphosphoranylideneamino)naphthalene **6b** (0.69 g, 1.5 mmol) in anhydrous toluene (20 ml) a solution of diphenylketene

(0.44 g, 2.25 mmol) in the same solvent (5 ml) was added. The reaction mixture was stirred at room temperature for 10 min, and then heated at reflux temperature for 1 h. After cooling at room temperature, the solvent was removed under reduced pressure and the crude material was chromatographed on a silica gel column, using hexanes/diethyl ether (20:1, v/v) as eluent, upto the total elution of **8b**, and then hexanes/diethyl ether (9:1, v/v).

We could not separate chromatographically compound **8b** from an unidentified impurity. Thus, after removing the solvent from the fractions containing compound **8b** the residue was treated with diethyl ether (4 ml), from which pure **8b** crystallized.

4.8.1. 7-Methyl-13-phenyl-7,7a,8,14-tetrahydrodibenz[*b*,*h*]acridine (8b). Yield 14%. Mixture of two diastereoisomers (1:1). ^{1}H NMR ($CDCl_3$) δ=1.26 (d, 3H, J=7.0 Hz), 1.57 (d, 3H, J=6.1 Hz), 2.76 (dd, 1H, J=15.2, 6.6 Hz), 2.97–3.09 (m, 4H), 3.18–3.21 (m, 1H), 3.30 (t, 1H, J=15.2 Hz), 3.44–3.52 (m, 1H), 6.51 (dd, 1H, J=7.6, 1.4 Hz), 6.56 (dd, 1H, J=7.6, 1.2 Hz), 6.77 (s, 1H), 6.88 (s, 1H), 6.90–7.01 (m, 3H), 7.07–7.13 (m, 4H), 7.16–7.49 (M, 15H), 7.60 (t, 4H, J=7.1 Hz), 7.70–7.72 (m, 2H). ^{13}C NMR ($CDCl_3$) δ=15.6, 16.5, 31.5, 34.4, 35.0, 35.3, 37.9, 41.1, 110.2 (s), 111.4 (s), 118.5, 118.6, 118.8, 119.1, 120.6 (s), 121.3 (s), 121.7 (s), 122.7, 122.8, 123.4, 123.6, 123.7, 123.8 (s), 125.2, 125.3, 125.4, 126.5, 126.6, 126.8, 127.0, 127.1, 127.2, 127.7, 128.6, 128.8, 129.9, 131.4, 131.5 (s), 132.0 (s), 132.2 (s), 133.1 (s), 133.3 (s), 133.4 (s), 136.5 (s), 137.0 (s), 137.1 (s), 137.5 (s), 137.9 (s), 138.0 (s). MS *m*/*z* (I%): 373 (M^+, 100). IR (nujol) ν cm^{-1}: 3436, 1620, 1594, 1564, 1296, 1275, 1210, 1191, 1109, 1041, 942, 926, 858, 804, 759, 743, 708. Anal. Calcd for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75. Found: C, 89.85; H, 6.29; N, 3.86.

4.8.2. 4-Methyl-3-(2,2-diphenylethyl)benzo[*h*]quinoline (13). Yield 17%; mp 197–198 °C; colorless prisms (diethyl ether). ^{1}H NMR ($CDCl_3$) δ=2.46 (s, 3H), 3.61 (d, 2H, J=7.7 Hz), 4.27 (t, 1H, J=7.7 Hz), 7.17–7.27 (m, 10H), 7.62–7.72 (m, 2H), 7.79 (d, 1H, J=9.1 Hz), 7.85–7.89 (m, 2H), 8.49 (s, 1H), 9.19–9.23 (m, 1H). ^{13}C NMR ($CDCl_3$) δ=14.3, 37.6, 52.7, 121.6, 124.6, 125.5 (s), 126.6, 127.0, 127.3, 127.6, 127.8, 128.1, 128.6, 131.8 (s), 131.9 (s), 132.9 (s), 141.7 (s), 143.9 (s), 144.6 (s), 150.7. MS *m*/*z* (I%): 373 (M^+, 16), 167 (100). IR (nujol) ν cm^{-1}: 1600, 1577, 1518, 1495, 1338, 827, 799, 753, 743, 727, 704. Anal. Calcd for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75. Found: C, 89.84; H, 6.29; N, 3.85.

4.9. Preparation of 13-phenyldibenz[*b*,*h*]acridines 14

To a solution of the corresponding 7,7a,8,14-tetrahydrodibenz[*b*,*h*]acridine **8** (150 mg) in *ortho*-xylene (5 ml) Pd/C (75 mg) was added, and the reaction mixture was heated at reflux temperature for 3 h. The hot solution was filtered over a short path of Celite, which was further washed with toluene (3×5 ml). The solvent was removed under reduced pressure an the resulting red solid was purified by column chromatography [silica gel; hexanes/diethyl ether (10:1, v/v)].

4.9.1. 13-Phenyldibenz[*b*,*h*]acridine (14a). Yield 97%; mp 202–203 °C; red prisms (diethyl ether). ^{1}H NMR ($CDCl_3$) δ=7.36–7.46 (m, 2H), 7.49 (d, 1H, J=9.3 Hz), 7.52–7.72 (m, 9H), 8.01–8.05 (m, 2H), 8.56 (s, 1H), 8.67 (s, 1H), 8.89–8.92 (m, 1H). ^{13}C NMR ($CDCl_3$) δ=124.7 (s), 125.4, 125.7, 125.8, 125.9, 126.6, 127.1, 127.3, 127.5, 127.6, 127.7, 127.8, 128.6, 129.3, 131.5 (s), 132.2 (s), 132.3 (s), 132.5, 134.0 (s), 134.9, 137.8 (s), 138.3 (s), 142.1 (s), 148.5 (s). FAB(+) *m*/*z* (I%): 356 (M^++1, 100). IR (nujol) ν cm^{-1}: 1631, 1594, 1329, 1308, 1157, 1140, 1123, 1073, 1009, 962, 922, 874, 845, 803, 755, 700, 692. Anal. Calcd for $C_{27}H_{17}N$: C, 91.24; H, 4.82; N, 3.94. Found: C, 91.09; H, 4.89; N, 3.99.

4.9.2. 7-Methyl-13-phenyldibenz[*b*,*h*]acridine (14b). Yield 82%; mp 213–214 °C; red prisms (diethyl ether). ^{1}H NMR ($CDCl_3$) δ=3.20 (s, 3H), 7.41 (ddd, 1H, J=7.8, 6.4, 1.3 Hz), 7.46–7.50 (m, 1H), 7.53–7.72 (m, 9H), 7.92 (d, 1H, J=9.5 Hz), 7.99–8.02 (m, 1H), 8.10–8.13 (m, 1H), 8.85 (s, 1H), 8.89–8.91 (m, 1H). ^{13}C NMR ($CDCl_3$) δ=14.1, 122.3, 122.7 (s), 123.4, 125.1 (s), 125.3, 126.0, 126.1, 127.0, 127.1, 127.3, 127.4, 127.5, 127.6, 129.0, 129.1, 131.3 (s), 131.9 (s), 132.6, 132.8 (s), 133.6 (s), 138.4 (s), 138.7 (s), 140.4 (s), 141.5 (s), 147.8 (s). FAB(+) *m*/*z* (I%): 370 (M^++1, 100). IR (nujol) ν cm^{-1}: 1557, 1543, 1509, 1157, 1074, 1027, 958, 869, 835, 792, 754, 738, 698, 681. Anal. Calcd for $C_{28}H_{19}N$: C, 91.02; H, 5.18; N, 3.80. Found: C, 90.81; H, 5.29; N, 3.88.

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References and notes

1. (a) Carruthers, W. Cycloaddition Reactions in Organic Synthesis; Pergamon: Oxford, 1990. (b) Fringuelli, F.; Taticchi, A. Dienes in the Diels–Alder Reaction; Wiley-Interscience: New York, 1990. (c) Oppolzer, W. In Trost, B. M., Fleming, I., Eds.; Comprehensive Organic Synthesis; Pergamon: Oxford, 1991; Vol. 5, pp 315–399. (d) Brocksom, T. J.; Nakamura, J.; Ferreira, M. L.; Brocksom, U. *J. Braz. Chem. Soc.* **2001**, *12*, 597–622.
2. (a) Evans, D. A.; Johnson, J. S. In Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Comprehensive Asymmetric Catalysis; Springer: Berlín, 1999; Vol. 3, pp 1177–1235. (b) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876–889. (c) Corey, E. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1650–1667.
3. Nicolaou, K. C.; Snyder, S. A.; Montagnon, T.; Vassiliko-ginnakis, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 1668–1698.
4. (a) Boger, D. L.; Weinreb, S. M. Hetero Diels–Alder Methodology in Organic Synthesis; Academic: San Diego, 1987. (b) Weinreb, S. M. In Trost, B. M., Fleming, I., Eds.; Comprehensive Organic Synthesis; Pergamon: Oxford, 1991; Vol. 5, pp 401–449. (c) Boger, D. L. In Trost, B. M., Fleming, I., Eds.; Comprehensive Organic Synthesis; Pergamon: Oxford, 1991; Vol. 5, pp 451–512. (d) Boger, D. L. *Tetrahedron* **1983**, *39*, 2869–2939. (e) Sakamoto, M.;

Kawasaki, T.; Ishii, K.; Tamura, O. *Yakugaku Zasshi* **2003**, *123*, 717–759.
5. (a) Stocking, E. M.; Williams, R. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 3078–3115. (b) Oikawa, H.; Tokiwano, T. *Nat. Prod. Rep.* **2004**, *21*, 321–352.
6. (a) Barker, M. W. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley-Interscience: Chichester, 1980; pp 701–720; part 2. (b) Dondoni, A. *Heterocycles* **1980**, *14*, 1547–1566. (c) Alajarín, M.; Vidal, A.; Tovar, F. *Targets Heterocycl. Syst.* **2000**, *4*, 293–326.
7. (a) Molina, P.; Alajarín, M.; Vidal, A. *Tetrahedron Lett.* **1991**, *32*, 5379–5382. (b) Molina, P.; Alajarín, M.; Vidal, A. *J. Org. Chem.* **1992**, *57*, 6703–6711.
8. Alajarín, M.; Vidal, A.; Tovar, F.; Conesa, C. *Tetrahedron Lett.* **1999**, *40*, 6127–6130.
9. Alajarín, M.; Vidal, A.; Ortín, M.-M.; Tovar, F. *Synthesis* **2002**, 2393–2398.
10. Alajarín, M.; Vidal, A.; Tovar, F. *Tetrahedron Lett.* **2000**, *41*, 7029–7032.
11. Methods for the synthesis of dibenz[*b*,*h*]acridines have been scarcely reported: (a) Buu-Hoï, N. P.; Jacquignon, P. *J. Chem. Soc.* **1951**, 2964–2968. (b) Étienne, A.; Staehelin, A. *Bull. Soc. Chim. Fr.* **1954**, 748–755.
12. (a) Sloviter, H. A. *J. Am. Chem. Soc.* **1949**, *71*, 3360–3362. For other preparations of **2a** and/or **2b** see: (b) Marcinkiewicz, S.; Green, J.; Mamalis, P. *Tetrahedron* **1961**, *14*, 208–222. (c) Inada, S.; Kurata, R.-i. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1581–1582. (d) Butsugan, Y.; Nagai, K.; Nagaya, F.; Tabuchi, H.; Yamada, K.; Araki, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1707–1714. (e) Shue, Y.-J.; Yang, S.-C.; Lai, H.-C. *Tetrahedron Lett.* **2003**, *44*, 1481–1485.
13. In the thermal treatment of the *N*-(2-propenyl)-1-naphthylamines **2**, the formation of other products besides the 2-(2-propenyl)-1-naphthylamines **3** was noted by Inada (see Ref. 12c), although these products were not isolated, and no mention to their putative structures was made.
14. Compound **5a**: (a) Gassman, P. G.; Schenk, W. N. *J. Org. Chem.* **1977**, *42*, 3240–3243. (b) Korda, A.; Wróbel, Z. *Synlett* **2003**, 1465–1466. Compound **5b**: (c) Babushkina, T. A.; Vasil'ev, A. M.; Shagalov, L. B.; Eraksina, V. N.; Tkachenko, T. A.; Suvorov, N. N. *Zh. Org. Khim.* **1975**, *11*, 864–871. (d) Tokunaga, M.; Ota, M.; Haga, M.-a.; Wakatsuki, Y. *Tetrahedron Lett.* **2001**, *42*, 3865–3868.
15. For a general review see: (a) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675–703. For a recent example of an hydroamination process based upon a well-defined calcium coordination complex see: (b) Crimmin, M. R.; Casely, I. J.; Hill, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 2042–2043. For examples of transition-metal complex-catalyzed cyclization of aminoalquenes see: (c) Hegedus, L. S. In Trost, B. M., Fleming, I., Eds.; Comprehensive Organic Synthesis; Pergamon: Oxford, 1991; Vol. 4, pp 551–569. (d) Tsuji, J. Palladium Reagents and Catalysts, Innovation in Organic Synthesis; Wiley: Chichester, 1995. (e) Hegedus, L. S.; Allen, G. F.; Waterman, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 2674–2676. (f) Hegedus, L. S.; Allen, G. F.; Bozell, J. J.; Waterman, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 5800–5807. For examples of actinide and lanthanide complex-catalyzed cyclization of aminoalquenes see: (g) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1757–1771. (h) Tian, S.; Arredondo, V. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1999**, *18*, 2568–2570. (i) Ryu, J.-S.; Marks, T. J.; McDonald, F. E. *Org. Lett.* **2001**, *3*, 3091–3094. (j) Molander, G. A.; Dowdy, E. D. *J. Org. Chem.* **1998**, *63*, 8983–8988. (k) Molander, G. A.; Dowdy, E. D. *J. Org. Chem.* **1999**, *64*, 6515–6517. (l) Kim, Y. K.; Livinghouse, T.; Bercaw, J. E. *Tetrahedron Lett.* **2001**, *42*, 2933–2935. (m) Stubbert, B. D.; Stern, C. L.; Marks, T. J. *Organometalllics* **2003**, *22*, 4836–4838. (n) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673–686.
16. Sreekimar, R.; Padmakumar, R. *Tetrahedron Lett.* **1996**, *37*, 5281–5282.
17. Yadav, J. S.; Reddy, B. V. S.; Rasheed, M. A.; Kumar, H. M. S. *Synlett* **2000**, 487–488.
18. To our knowledge only one example of thermally induced, intramolecular hydroamination of aminoalkenes has been described: (a) Molina, P.; Alajarín, M.; Vidal, A. *J. Chem. Soc., Chem. Commun.* **1990**, 7–8. (b) Molina, P.; Alajarín, M.; Vidal, A. *J. Org. Chem.* **1990**, *55*, 6140–6147.
19. For examples of thermally induced electrocyclization of 3-azatrienes see, for instance: (a) Palacios, F.; Rubiales, G. *Tetrahedron Lett.* **1996**, *37*, 6379–6382. (b) Beccalli, E. M.; Clerici, F.; Gelmi, M. L. *Tetrahedron* **2000**, *56*, 4817–4821.
20. Goerdeler, J.; Lindner, C.; Zander, F. *Chem. Ber.* **1981**, *114*, 536–548.
21. Morel, G.; Marchand, E.; Foucaud, A. *J. Org. Chem.* **1985**, *50*, 771–778.
22. Ramana Rao, V. V.; Fulloon, B. E.; Bernhardt, P. V.; Koch, R.; Wentrup, C. *J. Org. Chem.* **1998**, *63*, 5779–5786.
23. Alajarín, M.; Molina, P.; Vidal, A.; Tovar, F. *Tetrahedron* **1997**, *53*, 13449–13472.
24. Taylor, E. C.; McKillop, A.; Hawks, G. H. *Org. Synth.* **1973**, *52*, 36–38.
25. Pracejus, H.; Wallura, G. *J. Prakt. Chem.* **1962**, *19*, 33–36.