Found: C, 63.70; H, 5.49. (*Z*)-**28** was not obtained in a pure form and its ^{1}H NMR spectrum was extracted from that of a 1:1 (*E*)-**28**/(*Z*)-**28** mixture: ($CDCl_3$) δ 1.46 (9 H, s, COOBu-*t*), 2.21 (3 H, s, Me), 3.68 (3 H, s, COOMe), 6.82, 6.97 (4 H, AB q, J = 8.8 Hz, OTol), 7.58, 8.14 (4 H, AB q, J = 8.8 Hz, *p*-$O_2NC_6H_4$).

Acknowledgment. We are indebted to Dr. S. Cohen for the X-ray diffractions, and to the Israel Commission for Basic Research, The Israel Academy for Sciences and Humanities, who supported this work.

Supplementary Material Available: Tables S1–S16 giving the crystallographic data (bond lengths and angles, positional and thermal parameters) for (*E*)-**6**, (*Z*)-**19**, (*RR*)-**20**, and (*E*)-**21** and Figures S1–S4 giving their stereoscopic views (20 pages). Ordering information is given on current masthead page.

A New Synthesis of Indoles by Electrocyclic Ring Closure of Dialkenylpyrroles. Synthesis of Alkenylpyrroles from 1-Tosylalkenyl Isocyanides and Michael Acceptors[1]

Janusz Moskal and Albert M. van Leusen*

Department of Organic Chemistry, Groningen University, Nijenborgh 16, 9747 AG Groningen, The Netherlands

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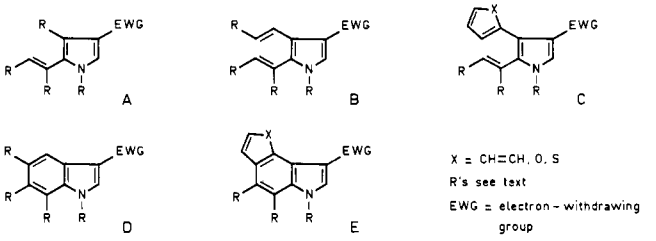
Addition of allylic anions derived from 1-tosylalk-1-enyl isocyanides **1** to Michael acceptors, in combination with ring closure to the isocyano carbon, provides a highly efficient synthesis of 2-alk-1′-enylpyrroles (types A–C). A proper selection of Michael acceptors permits the introduction of additional alkenyl or aryl substituents at C-3 and/or C-4 of the pyrrole ring (types B and C). Thermal or photochemical electrocyclization of 2,3-dialk-1′-enylpyrroles B, followed by dehydrogenation (DDQ), gives indoles D in excellent yields. Photochemical electrocyclization of 2-alk-1′-enyl-3-arylpyrroles C, together with dehydrogenation, provides an important extension of this synthesis to fused indole derivatives E.

The indole ring system constitutes the characteristic core of a great number of natural products, among which are the well-known indole alkaloids.[2] Thus, a new method to construct the indole ring may well be of advantage to the art of natural product synthesis. It is the purpose of this paper to describe an attractive new indole synthesis that is the result of two achievements: (1) a highly efficient new synthesis of monoalk-1′-enyl- and dialk-1′-enylpyrroles (types A–C; eq 1, Table I) and (2) an equally efficient electrocyclic ring closure of 2,3-dialk-1′-enylpyrroles (types B and C), followed by aromatization to the desired indoles (D and E; eqs 2 and 3, Tables II and III, respectively).

Indoles have been synthesized almost exclusively by constructing the pyrrole ring on to a benzene nucleus. Several classical methods are available to serve this purpose (Fischer, Madelung, and Reissert indole syntheses and the like).[3] The alternative of building a benzene ring on to a pyrrole has hardly been employed.[4] An obvious and potentially simple indole synthesis of this type would consist in the electrocyclization of pyrrole derivatives of type B and C, followed by dehydrogenation. This approach to indoles, however, has never been realized. The reason for this, evidently, is the lack of a good synthesis of the precursor pyrroles B and C.

Pyrroles with alk-1-enyl substitutents at the pyrrole ring carbons are uncommon among the large variety of known pyrrole derivatives.[5] Such alkenylpyrroles have been obtained from pyrrolecarboxaldehydes by Knoevenagel-type condensations.[6] Occasionally, other methods have been used, such as Wittig reactions[4a,b,7] or catalytic dehydrogenation of alkylpyrroles.[8] However, these methods are of limited scope, partly because the starting materials are not always easy to obtain. Anyhow, pyrroles of type B and C with two unsaturated substituents (at C-2 and C-3) have not been reported previously.



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(3) (a) For a brief introduction: Paquette, L. A. *Modern Heterocyclic Chemistry*; Benjamin: New York, 1968. (b) For a more complete coverage, see ref 2.

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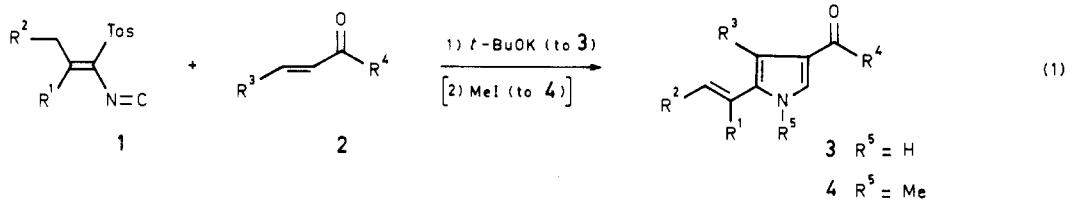
Table I. Pyrroles 3 and 4 Synthesized according to Equation 1

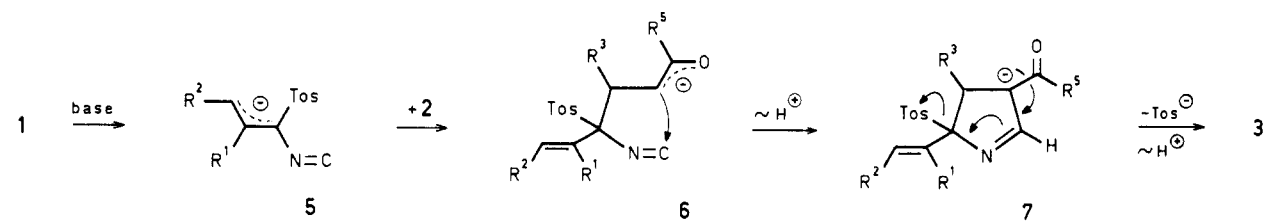


(1)

entry[a]	product	type	R^1	R^2	R^3	R^4	R^5	yield,[b] %	mp, °C
1*	**3a**	C		$(CH_2)_3$	Ph	Ph	H	95	217–218
2	**3b**	A		$(CH_2)_3$	Me	MeO	H	84	132–133
3	**3c**	C		$(CH_2)_3$	2-furyl	2-furyl	H	93	185–186
4	**3d**	A		$(CH_2)_4$	H	Me	H	96	150–151
5	**3e**	A		$(CH_2)_4$	H	MeO	H	83	139–140
6	**3f**	C		$(CH_2)_4$	Ph	MeO	H	95	211–212
7	**3g**	C		$(CH_2)_4$	Ph	(*E*)-PhCH=CH	H	96	183–184
8*	**3h**	B		$(CH_2)_4$	(*E*)-MeCH=CH	EtO	H	ca. 20[c]	oil
9	**3i**	B		$(CH_2)_4$	(*E*)-PhCH=CH	Ph	H	91	208–209
10	**3j**	C		$(CH_2)_4$	2-thienyl	2-thienyl	H	85	195–196
11	**3k**	C		$(CH_2)_5$	2-furyl	Ph	H	89	144–145
12	**3l**	A	Me	H	H	Me	H	88	95–96
13	**3m**	A	Me	H	H	MeO	H	90	93–94
14	**3n**	C	Me	H	Ph	Ph	H	95	209–210
15	**3o**	B	Me	H	(*E*)-PhCH=CH	Ph	H	96	138–139
16	**3p**	B	Ph	H	(*E*)-PhCH=CH	Me	H	92	193–194
17*	**4a**	B		$(CH_2)_3$	(*E*)-PhCH=CH	Ph	Me	84	141–142
18	**4b**[d]	C		$(CH_2)_3$	Ph	Ph	Me	84	156–157
19	**4c**[d]	B		$(CH_2)_4$	(*E*)-PhCH=CH	Ph	Me	91	150–151
20	**4d**	B		$(CH_2)_4$	(*E*)-PhCH=CH	MeO	Me	90	81–83
21	**4e**[d]	C		$(CH_2)_4$	2-thienyl	2-thienyl	Me	94	108–110
22*	**4f**[e]	B		$(CH_2)_4$	(*E*)-PhCH=CH	Ph	MeCO	82	168–170
23	**4g**	B		$(CH_2)_5$	(*E*)-PhCH=CH	Me	Me	87	109–110
24	**4h**	B		$(CH_2)_5$	(*E*)-PhCH=CH	Ph	Me	87	155–156
25	**4i**	B		$(CH_2)_6$	(*E*)-PhCH=CH	Ph	Me	83	137–138
26	**4j**	C		$(CH_2)_5$	2-furyl	Ph	Me	93	oil (n^{24}_D 1.605)
27	**4k**	B		$(CH_2)_{10}$	(*E*)-PhCH=CH	Ph	Me	82	164–165
28	**4l**[d]	B	Me	H	(*E*)-PhCH=CH	Ph	Me	90	136–137

[a] Typical procedures are given in full detail of entries marked with an asterisk. Selected spectral data of all pyrroles 3 and 4 are given in Table IV (see Experimental Section). [b] Overall yields of purified products based on compounds 1. [c] In addition to compound **3h**, the isomer formed by reaction with C-γ, C-δ, i.e. (4-(2′-carbethoxyeth-1′-enyl)-2-cyclohex-1′-enyl-3-methylpyrrole (**8**, mp 136–137 °C) was obtained in 55% yield. See also ref 16. [d] Compounds **4b**, **4c**, **4e**, and **4l** are the N-methyl derivatives of compounds **3a**, **3i**, **3j**, and **3o**, respectively. [e] Compound **4f** is the *N*-acetyl derivative of **3i**, that is R^5 = MeCO (rather than Me as is indicated in eq 1).

Scheme I



Synthesis of Alk-1-enylpyrroles. Pyrroles of type A–C are synthesized by a base-induced cycloaddition of 1-tosylalk-1-enyl isocyanide **1** to a Michael acceptor **2** (eq 1, Table I). In this process the pyrrole ring is constructed by formation of the C-2,C-3 and C-4,C-5 bonds.[9] This is achieved in one operation from equimolar quantities of reactants. It is an attractive new synthesis of 2,4-disubstituted and 2,3,4-trisubstituted pyrroles, in which one or more of the substituents are of the alk-1-enyl type (A–C).

The reactants of eq 1 are readily available. 1-Tosylalk-1-enyl isocyanides **1** are easily obtained by (a formal) condensation[10] of commercially available starting materials: tosylmethyl isocyanide (TosMIC)[11] and carbonyl compounds. Michael acceptors are commercially available in variety or readily accessible otherwise.

The overall results of eq 1 are rationalized in Scheme I. Addition of allylic anion **5** to Michael acceptor **2** followed by ring closure of enolate anion **6** (to the isocyano carbon) and elimination of *p*-toluenesulfinate (Tos^-) gives pyrrole **3**.[12] The allylic anion **5**, formed by γ-deprotona-

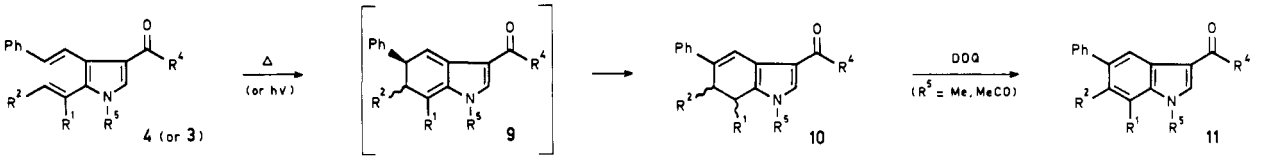
(9) A related synthesis of pyrroles from Michael acceptors and tosylmethyl isocyanide (TosMIC)[11] was reported earlier by our research group: van Leusen, A. M.; Siderius, H.; Hoogenboom, B. E.; van Leusen, D. *Tetrahedron Lett.* **1972**, 5337. Possel, O.; van Leusen, A. M. *Heterocycles* **1977**, *7*, 77. Reference 11.

(10) Via dehydrogenation of the corresponding formamides: van Leusen, A. M.; Schaart, E. J.; van Leusen, D. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 258. Gist-brocades, European Patent Application Nb. 0007672. By a Peterson olefination: van Leusen, A. M.; Wildeman, J. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 202.

(11) Reviews: van Leusen, A. M. *Lect. Heterocycl. Chem.* **1980**, *5*, S111. van Leusen, A. M. *Proceedings of the 12th International Symposium on the Organic Chemistry of Sulfur*; Elsevier: Amsterdam, 1986; in press.

(12) A synchronous or concerted cycloaddition rather than a stepwise process is also possible, cf. ref 9.

Table II. Indoles 11 and Dihydroindoles 10 Synthesized according to Equation 2



entry[a]	start. mat.[b]	R^1	R^2	R^4	R^5	product	yield,[c] %	mp, °C
1	**4a**	$(CH_2)_3$		Ph	Me	**10a**	92	148–151
2*	**4c**	$(CH_2)_4$		Ph	Me	**10b**	96	168–170
3*	**3i**	$(CH_2)_4$		Ph	H	**10c**	94	251–254
4*	**4l**	Me	H	Ph	Me	**10d**[d]	87[d]	75–79
5*	**4a**	$(CH_2)_3$		Ph	Me	**11a**	83[e]	172–173
6	**4c**	$(CH_2)_4$		Ph	Me	**11b**	95[e]	177–178
7	**4h**	$(CH_2)_5$		Ph	Me	**11c**	92[e]	186–187
8	**4i**	$(CH_2)_6$		Ph	Me	**11d**	84	206–207
9	**4k**	$(CH_2)_{10}$		Ph	Me	**11e**[f]	89	186–187[f]
10	**4g**	$(CH_2)_5$		Me	Me	**11f**	90	192–193
11	**4d**	$(CH_2)_4$		MeO	Me	**11g**	86	156–157
12*	**4l**	Me	H	Ph	Me	**11h**	90	164–165
13*	**4f**	$(CH_2)_4$		Ph	H	**11i**[g]	31[g]	233–234
14*	**11b**	$(CH{=}CH)_2$		Ph	Me	**11j**[h]	98	238–239

[a] Typical procedures are given of entries marked with an asterisk. Selected spectral data of all indoles **10** and **11** are given in Table V (see Experimental Section). [b] Numbers of starting pyrroles, which are listed in Table I. [c] Yields of isolated products from thermal ring closures (compounds **10**), plus one-pot dehydrogenation (compounds **11**), always calculated from **4** (or **3**). [d] Mixture (ca. 1:1) of 6,7-dihydroindole **10d** and the 4,5-dihydro isomer, according to ^1H and ^{13}C NMR. [e] Yields obtained via photochemical ring closure and dehydrogenation are 84% (**11a**), 92% (**11b**), and 91% (**11c**). [f] Crystallizes frequently with one molecule of water, in which case the mp is 167–168 °C. [g] A second indole was isolated (48%, mp 207–208 °C) to which we have assigned tentatively the following structure **11i** with an acetyl substituent at C-2 (see Experimental Section). It is assumed that the acetyl is shifted from N to C-2 during the treatment with DDQ. [h] Prepared from **11b** and 2.2 equiv of DDQ.

tion of **1**, appears to react exclusively at C-α,[13] to form ultimately the alkenyl substituent at C-2 in pyrrole **3**.

Table I provides over 20 examples of this novel pyrrole synthesis. The pyrroles **3** (R^5 = H) are obtained in excellent yields (around 90% of purified product) using *t*-BuOK in THF (entries 1–16). Often, crude reaction products were converted to *N*-methyl derivatives **4** (R^5 = Me, entries 17, 20, 23–27), and characterized as such. In some cases both the *N*-hydropyrroles **3** and the *N*-methylpyrroles (or *N*-methylcarbonylpyrroles) **4** were identified individually (entries 1, 9, 10, 15 and 18, 19, 21, 22, 28, respectively).

Our pyrrole synthesis works equally well with tosylalkenyl isocyanides **1** derived of cyclic ketones (entries 1–11, 17–27) as with those derived of noncyclic ketones (entries 12–16, 28). With both categories of reagents **1** only one pyrrole **3** (or **4**) was obtained by a regiospecific reaction with the C,C double bond of α,β-unsaturated ketones or esters (entries 1–6, 10–14, 26).[14] Pyrrole **3g** was obtained in 96% yield by reaction of one of the double bonds of 1,5-diphenylpenta-1,4-dien-3-one (dibenzalacetone) using 1 equiv of reagent **1** (R^1,R^2 = $(CH_2)_4$, entry 7).[15]

More important is the fact that only one pyrrole was formed (in high yield) by a site-specific and regiospecific reaction with the C-α,C-β double bond of the conjugated system of ketones PhCH=CHCH=CHCOR (R = Ph, Me, entries 9, 15–17, 19, 22–25, 27, 28). These reactions thus provide 2,3-dialk-1′-enylpyrroles (type B) which play a crucial role in the new indole synthesis described below.

The results with esters RCH=CHCH=CHCOOR are less straightforward. Although pyrrole **4d** was obtained as the only product (72% yield) from methyl 5-phenyl-2,4-pentadienoate (methyl cinnamylideneacetate) by reaction with the C-α,C-β double bond (entry 20), ethyl sorbate gave in a non-site-specific reaction a mixture of two pyrroles, of which the 2,3-disubstituted pyrrole **3h** was the minor product (entry 8).[16]

The regiospecific addition of **1** to chalcone-type substrates aryl—CH=CHCOR provided 2-alk-1′-enyl-3-arylpyrroles (type C, entries 3, 6, 7, 10, 11, 14, 18, 21, 25), which are precursors to fused indole derivatives (type E).

All reactions of Table I were carried out with *t*-BuOK in THF. The reaction of entry 9 was used to vary conditions. Identical results were obtained with *t*-BuOK in DME (90% yield of **3i**). The yield of **3i** was some 10% lower when NaH was used in Me_2SO/Et_2O and about 20% lower with *n*-BuLi in THF. No reaction was observed under phase-transfer conditions (50% NaOH, CH_2Cl_2 or benzene, $PhCH_2NEt_3Cl$).

Under standard conditions (*t*-BuOK, THF), reagent **1** [R^1,R^2 = $(CH_2)_4$] gave no reaction with diethyl acetylenedicarboxylate, whereas complex mixtures were obtained with maleic anhydride and with 4-benzoquinone.

Synthesis of Indoles (Type D) from 2,3-Dialk-1′-enylpyrroles. The six (or ten) π-electron system of pyrroles of type B (Table I) is nicely set up for an electrocyclic ring closure.[17] This process, in combination with dehydrogenation of the initially formed dihydroindoles **10**, is the basis of a new and efficient synthesis of indoles **11** (eq 2, Table II).

(13) Precedent for such behavior was reported recently: Moskal, J.; van Leusen, A. M. *Tetrahedron Lett.* **1984**, *25*, 2585. van Leusen, D.; van Leusen, A. M. *Ibid.* **1984**, *25*, 2581.

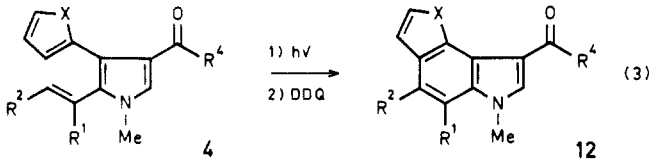
(14) Compare ref 9. It should be noted that Li_2 TosMIC reacts specifically with the *ester* group of α,β-unsaturated esters to form oxazoles: van Nispen, S. P. J. M.; Mensink, C.; van Leusen, A. M. *Tetrahedron Lett.* **1980**, *21*, 3723.

(15) No attempts were made to convert both C,C double bonds of dibenzalacetone into pyrrole rings with 2 equiv of the same reagent.

(16) A mixture of the same two isomers was obtained in a ratio **3h**/**8** = 38/62 (60% yield) with BuLi in THF (for structure of **8** see footnote *c* of Table I). Furthermore, an analogous mixture of isomers (ratio 4/6, 83% yield) was obtained from ethyl sorbate and (isocyanotosylmethylidene)cyclooctane.

(17) Leading reference to carbocyclic analogues of this electrocyclization: Marvell, E. N. *Thermal Electrocyclic Reactions*; Academic: New York, 1980; Chapter 7. Furthermore, there is one report of a successful thermal electrocyclization of 2,3-dialk-1′-enylindoles in the presence of Pd/C to give carbazoles (21–49% yield): Kano, S.; Sugino, E.; Shibuya, S.; Hibino, S. *J. Org. Chem.* **1981**, *46*, 3856. And, more recently, one unsuccessful attempt: Jones, R. A.; Fresneda, P. M.; Saliente, T. A.; Arques, J. S. *Tetrahedron* **1984**, *40*, 4837.

Table III. Fused Indole Derivatives 12 Synthesized according to Equation 3



entry[a]	start. mat.[b]	R^1,R^2	R^4	X	product	yield,[c] %	mp, °C
1*	**4b**	$(CH_2)_3$	Ph	CH=CH	**12a**	76	148–149
2*	**4e**	$(CH_2)_4$	2-thienyl	S	**12b**	78	205–206
3*	**4j**	$(CH_2)_5$	Ph	O	**12c**	73	207–209

[a] Typical procedures are given in full detail of entries marked with an asterisk. Selected spectral data are given in Table V (see Experimental Section). [b] Numbers of starting materials, which are listed in Table I. [c] Overall yield of isolated products based on **4**.

Table II collects the results of thermal ring closures carried out in boiling triglyme (triethylene glycol dimethyl ether, bp 216 °C; 1 h). The resulting dihydroindoles **10** can be isolated in pure state simply by workup with water. Four dihydroindoles were thus characterized (**10a–d**, entries 1–4). For practical purposes, however, the dehydrogenations to indoles **11** were carried out without isolating the dihydroindoles **10** in a one-pot procedure (triglyme, DDQ, 80 °C, 1 h, entries 5–14).

Thermal ring closure is possible for pyrroles with a free NH group (R^5 = H, entry 3), the dehydrogenation step, however, requires N-protection (R^5 = Me, MeCO, entries 5–14). The *N*-acetyl protective group was removed by hydrolysis afterwards to form indole **11i** (entry 13). The low yield of **11i** (31%) is due to an acetyl shift to C-2 which probably took place during the reaction with DDQ.[18]

Furthermore, we have shown that the tetrahydrobenzindole derivative **11b** can be dehydrogenated further to the fully aromatized benzo[*g*]indole **11j**.

Ring closure of 2,3-dialkenylpyrroles can be achieved photochemically also, as was shown for indoles **11a–c**. The photochemical electrocyclization was carried out at room temperature in cyclohexane with 3–5% of ethanol (high-pressure UV immersion lamp, Hanau TQ 150, 12 h) to give nearly the same yields as in the thermal reactions (entries 5–7). The pyrrole NH needs protection in the photochemical ring closure. For synthetic purposes, the thermal process is more convenient.

The conversion of **4** (and **3**) to **10** (eq 2) involves electrocyclic ring closure and a 1,5-sigmatropic shift of hydrogen. On the basis of a synchronous concerted process and the orbital symmetry rules,[19] one expects for compounds **10** a cis ring fusion at C-6,C-7. Unfortunately, NMR analysis of the dihydroindoles **10a–d** does not allow an unambiguous stereochemical assignment. The reactions of entries 1–3 of Table II gave each a single product in which R^1,R^2 are part of a five- or six-membered ring (**10a–c**, 86–96%). These compounds clearly are 6,7-dihydroindoles on the basis of ^{13}C NMR (two doublets at δ 51 and 48). However, the ^1H NMR multiplets (δ 2.5–3.0) are too complex to determine H-6,H-7 coupling constants. The reaction of entry 4 gave a 1:1 mixture of two dihydroindoles: the 6,7-dihydroindole **10d** and its 4,5-dihydro isomer (R^1 = CH_3, R^2 = H). We tentatively explain the formation of only one dihydro isomer in case of a cyclic R^1,R^2 substituent (entries 1–3) to secondary thermal isomerization processes governed by larger differences in thermodynamic stability of the 6,7- vs. 4,5-dihydro isomers.

(18) See footnote *g* of Table II.

(19) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim 1970; Chapter 5. Fleming, I. *Frontier Orbitals and Organic Reactions*; Wiley: London, 1976. *Thermal Electrocyclic Reactions*; Academic: New York, 1980; Chapter 2.

Synthesis of Indoles (Type E) from 2-Alk-1′-enyl-3-arylpyrroles. An important extension of our indole synthesis has been realized by using pyrroles of type C (Table I). Table III gives three examples of this extension, which differ from the reactions of eq 2 in that the two participating π-electrons of the substituent at C-3 are now part of a benzene, a thiophene, or a furan ring. In these cases the electrocyclic ring closure has to be carried out photochemically (20 °C, 12 h) on N-protected pyrroles. For the rest, these reactions show great similarity to those of the previous section.

All indoles, as well as the pyrroles, described in this paper are new compounds. Apparently, our syntheses add to the chemistry of these heterocycles in that new substitution patterns have been made available.

Experimental Section

Full experimental details are given of a representative selection of procedures, which are marked with an asterisk in the entry columns of Tables I–III. Selected spectral data of the other products are collected in Tables IV and V; more information is available as supplementary material.

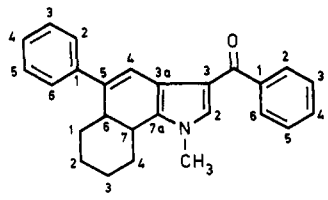
General. All reactions were carried out under nitrogen. When so needed, the temperature of reaction mixtures was kept between −50 and −60 °C by occasionally adding liquid nitrogen to a ca. 3 cm thick layer of cotton wool that was applied to the wall of the reaction vessel. The photoelectrocyclizations were performed with a high-pressure HANAU TQ 150 mercury quartz immersion lamp, and a reaction vessel equipped with a quartz filter. ^1H NMR spectra were recorded with a 60-MHz Hitachi Perkin-Elmer R-24B spectrometer; ^{13}C NMR spectra were determined on a Varian XL-100 (FT) or a Nicolet 200 instrument and are recorded in δ (ppm) units downfield from Me_4Si. The reported multiplicity of ^{13}C NMR signals is based on $^1J_{CH}$ coupling only. IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer in KBr pellets. An AEI 902 spectrometer was used for determination of the mass spectra (DI system; e.v. 70 eV; acc. v. 8 kV; multiplier 2.1 kV; I.S. temperature 120 °C; D.I. temperature 120–150 °C). Combustion microanalyses were carried out in the Analytical Department of our laboratory (A. F. Hamminga, J. Ebels, H. Draayer, J. E. Vos).

Starting Materials. The synthesis of unsaturated tosyl isocyanides **1** was reported.[10] Commercially available α,β-unsaturated carbonyl compounds were purified by crystallization or distillation before use. The others were prepared by published methods. Potassium *tert*-butoxide (*t*-BuOK, specified quality at least 97%), benzyltriethylammonium chloride (TEBACl), and 2,3-dichloro-5,6-dicyanoquinone (DDQ) (all purchased from Merck) were used as such.

Solvents. Tetrahydrofuran (THF) was distilled from $LiAlH_4$; benzene, *n*-hexane, cyclohexane, and triglyme (1,2-bis(2-methoxyethoxy)ethane) (all purchased from Merck) were dried and distilled before use.

The chemical names are given following IUPAC rules. To facilitate the notation of ^{13}C NMR data in the Experimental Section and the supplementary material an unofficial numbering is adopted, i.e., the pyrrole and the indole cores are numbered according to normal conventions, the carbons of the substituents

are numbered independently as shown, for example, for **10a**. The



10a

assignment of the carbon signals is based on the multiplicity of direct and long-range C,H couplings, the increment system for substituted benzenes,[20] and comparison with reported data.[21] The one-bond C,H coupling constants of the phenyl ring carbons are in the range of 160.0–162.5 Hz; they are not reported individually.

4-Benzoyl-2-cyclopent-1′-enyl-3-phenylpyrrole (3a). To a suspension of *t*-BuOK (1.12 g, 10 mmol) in 15 mL of THF, precooled to −60 °C, was added slowly (ca. 15 min) a solution of (isocyanotosylmethylidene)cyclopentane[10] (1, R^1,R^2 = $(CH_2)_3$, 2.61 g, 10 mmol) in 20 mL of THF to maintain the temperature between −60 and −50 °C. The reaction mixture turned to a transparent orange solution, which was stirred for an additional 10 min at −50 °C before a solution of 1,3-diphenylprop-1-en-3-one (chalcone, 2.08 g, 10 mmol) in 20 mL of THF was added dropwise (ca. 10 min). The temperature of the reaction mixture increased to −20 °C. When stirring was continued for 1 h without further cooling, a precipitate was formed. The reaction mixture was poured into 250 mL of cold water and stirred for 30 min. Yellow-orange crystals were collected (3.2 g), washed with water, and purified by crystallization from EtOH to give 2.98 g (95%) of **3a**: mp 217–218 °C; IR 3230 (NH), 3140, 1610 (C=O), 1508, 1485, 1440 cm^{-1}; ^1H NMR [$(CD_3)_2SO$] δ 10.11 (br, s, 1, NH), 7.7–6.9 (m, 11), 5.6–5.7 (m, 1), 2.2–2.0 (m, 4), 2.0–1.5 (m, 2); ^{13}C NMR [$(CD_3)_2SO$] δ(benzoyl) 128.1 (d, C-3, C-5), 128.7 (d, C-2, C-6), 131.2 (d, C-4), 140.1 (s, C-1), δ(cyclopentenyl) 22.9 (t, J = 128.7 Hz, C-4), 32.3 (t, J = 131 Hz, C-3), 33.6 (t, J = 128.2 Hz, C-5), 122.8 (s, C-1), 125.4 (d, J = 155.8 Hz, C-2), δ(pyrrole) 122.7 (s, C-3), 126.6 (d, J = 186.4 Hz, C-5), 128.3 (s, C-2), 134.1 (s, C-4), δ(phenyl) 126.1 (d, C-2, C-6), 127.2 (d, C-4), 130.6 (d, C-3, C-5), 136.3 (s, C-1); δ 189.7 (s, C=O); mass spectrum, m/z (relative intensity) 313 (M^+, 93.7), 314 (22.8), 312 (12.7), 284 (11.5), 236 (8.9), 208 (27.4), 180 (24.8), 105 (100), 77 (32.6). Anal. Calcd for $C_{22}H_{19}NO$ (313.15): C, 84.35; H, 6.07; N, 4.47. Found: C, 84.08; H, 6.08; N, 4.44.

4-Carbethoxy-2-cyclohex-1′-enyl-3(*E*)-prop-1′-enylpyrrole (3h) and 4-[(*E*)-2′-Carbethoxyeth-1′-enyl]-2-cyclohex-1′-enyl-3-methylpyrrole (8). To a suspension of *t*-BuOK (1.12 g, 10 mmol) in 15 mL of THF, precooled to −40 °C, was added dropwise a solution of (isocyanotosylmethylidene)cyclohexane[10] (1, R^1,R^2 = $(CH_2)_4$, 2.75 g, 10 mmol) in 20 mL of THF (ca. 15 min) to maintain the temperature of the reaction mixture below −30 °C. The reaction mixture became a transparent orange solution, which was stirred for an additional 10 min before a solution of ethyl sorbate (1.40 g, 10 mmol) in 10 mL of THF was added slowly (ca. 10 min). The temperature increased to −10 °C. Stirring was continued for 1 h without further cooling. After 15 min a precipitate began to appear. The reaction mixture was poured into 150 mL of cold water, stirred for 30 min, and then extracted with CH_2Cl_2 (2 × 50 mL). The organic layers were combined, dried ($MgSO_4$), and concentrated. The dark greenish oily residue (2.1 g) was chromatographed over alumina (Brockmann 90, II/III; 250 g) using a mixture of dichloromethane and *n*-pentane (1:1) as eluent. From the first two fractions 0.4 g (20%) of **3h** was obtained as unstable yellow greasy crystals, which turned rapidly into a green-blue oil. The third fraction contained 1.43 g (55%) of 8 as pale yellow crystals: mp 136–137 °C (from ethanol). Pyrrole **3h**: IR 3370 (NH), 1700 (C=O), 1612 (C=C), 1445, 1270 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.30 (s, 1, NH), 8.05 (d, J = 2.9 Hz, 1), 6.81 (d, J = 13.3 Hz, 1), 5.8–5.7 (m, 1), 5.33 (d, J = 13.3 Hz, 1), 4.08 (q, J = 7.3 Hz, 2), 2.11 (d, J = 1.2 Hz, 3), 2.3–2.1 (m, 4), 1.8–1.6 (m, 4), 1.22 (t, J = 7.3 Hz, 3). Pyrrole 8: IR 3320 (NH), 1680 (C=O), 1615 (C=C), 1480, 1450, 1285 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.30 (s, 1, NH), 7.55 (d, J = 16.0 Hz, 1), 6.85 (d, J = 2.7 Hz, 1), 5.95 (d, J = 16.0 Hz, 1), 5.8–5.7 (m, 1), 4.18 (q, J = 7.2 Hz, 2), 2.18 (s, 3), 2.2–2.1 (m, 4), 1.7–1.6 (m, 4), 1.30 (t, J = 7.2 Hz, 3); ^{13}C NMR ($CDCl_3$) δ(cyclohexenyl) 21.9 (t, J = 124.6 Hz, C-4), 22.6 (t, J = 125.6 Hz, C-5), 25.2 (t, J = 129.6 Hz, C-3), 27.7 (t, J = 125.6 Hz, C-6), 120.3 (s, C-1), 125.6 (d, J = 155.4 Hz, C-2), δ(pyrrole) 114.1 (s, C-3), 118.5 (d, J = 187.5 Hz, C-5), 128.9 (s, C-2), 132.5 (s, C-4), δ(ethenyl) 112.1 (d, J = 160.6 Hz, C-1), 139.0 (d, J = 154.3 Hz, C-2), δ 11.2 (q, J = 126.6 Hz, CH_3), 14.2 (q, J = 127.6 Hz, CH_3CH_2), 59.8 (t, J = 139.6 Hz, CH_3CH_2), 168.3 (s, C=O); mass spectrum, m/z (relative intensity) 259 (M^+, 100), 260 (17.6), 258 (10.7), 230 (21.7), 215 (17.8), 186 (16.8), 169 (8.0), 156 (7.6), 144 (6.0), 28 (9.8). Anal. Calcd for $C_{16}H_{21}NO_2$ (259.16): C, 74.13; H, 8.11; N, 5.40. Found: C, 73.80; H, 8.22; N, 5.43.

4-Benzoyl-2-cyclopent-1′-enyl-3-[(*E*)-2′-phenylethenyl]-1-methylpyrrole (4a). To a suspension of *t*-BuOK (1.12 g, 10 mmol) in 15 mL of THF, precooled to −60 °C, was added dropwise a solution of (isocyanotosylmethylidene)cyclopentane[10] (1, R_1,R_2 = $(CH_2)_3$, 2.61 g, 10 mmol) in 20 mL of THF to maintain the temperature below −50 °C. The reaction mixture turned into a transparent orange solution, which was stirred for an additional 10 min at −50 °C. Then a solution of 1,5-diphenylpenta-1,3-dien-5-one (cinnamylideneacetophenone,[22] 2.34 g, 10 mmol) in 20 mL of THF was added. The temperature increased to −20 °C. Stirring was continued for 1 h without further cooling. Then the reaction mixture was concentrated in vacuum (at 20 °C), and the solid residue was suspended in 30 mL of benzene. To this suspension, methyl iodide (2.82 g, 20 mmol) was added, and the mixture as treated with 30 mL of 50% aqueous KOH containing 0.25 g of TEBACl. The reaction mixture was vigorously stirred for 1 h at room temperature. The benzene layer was separated, washed with 10% aqueous NH_4Cl (50 mL) and then twice with water (50 mL each), and dried ($MgSO_4$), to give 2.96 g (84%) of pale yellow crystals of **4a** after concentration and crystallization from EtOH: mp 141–142 °C; IR 2905, 2838, 1620 (C=O, C=C), 1500, 1420, 1345, 1221 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.7 (m, 2), 7.4–7.0 (m, 10), 6.89 (s, 1), 6.0–5.9 (m, 1), 3.48 (s, 3), 2.8–2.4 (m, 4), 2.3–1.8 (m, 2); ^{13}C NMR ($CDCl_3$) δ(benzoyl) 128.6 (d, C-2, C-6, C-3, C-5), 130.9 (d, C-4), 140.4 (s, C-1), δ(cyclopentenyl) 23.7 (t, J = 125.9 Hz, C-4), 33.0 (t, J = 129.8 Hz, C-5), 34.5 (t, J = 129.8 Hz, C-3), 120.6 (s, C-1), 130.8 (d, J = 160.8 Hz, C-2), δ(phenyl) 125.7 (d, C-2, C-6), 127.7 (d, C-4), 128.1 (d, C-3, C-5), 138.4 (s, C-1);, δ(ethenyl) 121.7 (d, J = 152.7 Hz, C-2), 126.3 (d, J = 156.9 Hz, C-1), δ(pyrrole) 120.5 (s, C-3), 128.5 (d, J = 185.6 Hz, C-5), 134.1 (s, C-2), 134.8 (s, C-4); δ 34.8 (q, J = 139.2 Hz, N-CH_3), 191.2 (s, C=O); mass spectrum, m/z (relative intensity) 353 (M^+, 79.2), 354 (20.6), 338 (15.4), 276 (9.6), 262 (18.1), 250 (12.8), 248 (53.2), 131 (11.8), 105 (100), 103 (15.4), 91 (36.2), 77 (24.9). Anal. Calcd for $C_{25}H_{23}NO$ (353.18): C, 84.99; H, 6.52; N, 3.97. Found: C, 85.00; H, 6.57; N, 4.00.

1-Acetyl-4-benzoyl-2-cyclohex-1′-enyl-3-[(*E*)-2′-phenylethenyl]pyrrole (4f). A solution of 4-benzoyl-2-cyclohex-1′-enyl-3-[(*E*)-2′-phenylethenyl]pyrrole (**3g**, 2.23 g, 6.6 mmol) in 15 mL of dry benzene was stirred for 15 min at room temperature with *t*-BuOK (0.74 g, 6.6 mmol). Then freshly distilled acetyl chloride (0.62 g, 7.0 mmol) in 10 mL of dry benzene was added, and stirring was continued for an additional 30 min. The precipitate was removed, and the benzene filtrate was concentrated. The solid residue (2.3 g) was purified by crystallization from benzene/*n*-pentane (2:1) to give 2.1 g (82%) of white crystals: mp 168–170 °C; IR 2930, 1750 (CH_3C=O), 1625 (PhC=O), 1375, 1335, 1195, 965 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.8 (m, 2), 7.5–6.9 (m, 11), 5.9–5.8 (m, 1), 2.45 (s, 3), 2.3–2.1 (m, 4), 1.9–1.6 (m, 4); exact mass

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Table IV. Selected Spectral Data of Pyrroles 3 and 4 of Table I

pyrrole		IR, cm^{-1}			^1H NMR, δ[a]			^{13}C NMR, δ[c]					MS, m/z (rel intensity)		
	type	$\nu_{NH(CH_3)}$	ν_{CO}	solvent	$NH(CH_3)$[b]	H-5	alkenyl H at C-2	C-2	C-3	C-4	C-5	C=O	M^+	$M^+ + 1$	base peak
3a	A	3230	1610	$(CD_3)_2SO$	10.11	6.94 d (3.0)	5.6–5.7 m	128.3	122.7	134.1	126.6 d (186.4)	189.7	313 (93.7)	314 (22.8)	105
3b	A	3310	1675	$CDCl_3$	8.50	7.21 d (2.9)	5.7–5.8 m	127.6	115.4	133.8	123.0 d (189.4)	166.0	205 (100)	206 (14.0)	205
3c	C	3250	1610	$(CD_3)_2SO$	11.15	7.30 d (2.4)	5.7–5.8 m	130.9	111.1	133.7	125.7 (189.8)	175.5	293 (100)	294 (21.0)	293
3d	A	3290	1630	$CDCl_3$	9.55	7.19 q_{AB} (3.0; $^4J_{HH}$ = 1.8)	5.8–5.9 m	128.1	103.8 d (170.5)	135.4	123.8 d (182.5)	194.2	189 (100)	190 (14.7)	189
3e	A	3215	1675	$CDCl_3$	8.78	7.15 q_{AB} (3.0; $^4J_{HH}$ = 1.8)	5.7–5.8 m	128.1	104.8 d (173.5)	134.7	123.5 d (187.3)	165.8	205 (100)	206 (12.4)	205
3f	C	3305	1675	$CDCl_3$	8.50	7.14 d (3.0)	5.6–5.7 m	129.6	114.4	135.5	123.0 d (183.0)	165.4	281 (100)	282 (19.4)	281
3g	C	3300	1580	$CDCl_3$	9.65	6.97 d (3.1)	5.5–5.6 m	126.0	120.6	135.2	123.2 d (182.5)	186.3	353 (100)	354 (29.9)	353
3h	B	3380	1700	$CDCl_3$	8.30	8.05 d (2.9)	5.7–5.8 m								
3i	B	3210	1590	$(CD_3)_2SO$	11.51	7.3–7.1[d]	5.7–5.8 m	129.9	117.6	134.6	127.2 d (186.9)	190.9	353 (46.3)	354 (11.8)	105
3j	C	3290	1603	$CDCl_3$	9.06	7.16 d (3.1)	5.7–5.8 m	128.6	113.1	134.6	123.8 d (189.9)	182.4	339 (59.9)	340 (14.5)	111
3k	C	3240	1610	$CDCl_3$	9.46	6.95 d (3.0)	6.05 t (7.2)	136.6	110.0	136.6	126.8 d (188.3)	191.6	331 (75.5)	332 (18.0)	105
3l	A	3250	1630	$CDCl_3$	9.80	7.25 q_{AB} (3.1; $^4J_{HH}$ = 1.8)	5.11 s [1 H] 4.81 s [1 H]	133.9	106.0 d (173.0)	134.8	125.1 d (185.7)	194.6	149 (61.8)	150 (6.3)	134
3m	A	3290	1685	$CDCl_3$	9.30	7.21 q_{AB} (3.2; $^4J_{HH}$ = 1.9)	5.08 s [1 H] 4.80 s [1 H]	133.9	107.3 d (173.8)	134.2	124.2 d (188.7)	165.5	165 (52.3)	166 (5.3)	134
3n	A	3260	1615	$(CD_3)_2SO$	10.52	7.3–7.2[d]	4.91 s [1 H] 4.86 m [1 H]	131.6	122.7	135.1	126.2 d (186.6)	189.9	287 (36.5)	288 (8.5)	105
3o	B	3260	1610	$CDCl_3$	9.20	7.3–7.0[d]	5.0–5.2 m [2 H]	133.3	119.5	136.2	122.9 d (188.1)	192.5	313 (61.5)	314 (15.1)	105
3p	B	3215	1625	$(CD_3)_2SO$	9.95	7.4–7.2[d]	5.50 s [1 H] 5.78 s [1 H]	131.4	118.7	139.1	127.4 d (185.6)	193.6	313 (60.3)	314 (18.2)	105
4a	B	2838	1620	$CDCl_3$	(3.48)	6.88	5.9–6.0 m	134.1	120.5	134.8	128.5 d (185.6)	191.2	353 (79.2)	354 (20.6)	105
4b	C	2830	1640	$CDCl_3$	(3.48)	6.94	5.8–5.6 m								
4c	B	2840	1625	$CDCl_3$	(3.40)	6.71	5.9–5.7 m						367 (9.1)	368 (2.7)	105
4d	B	2840	1640	$CDCl_3$	(3.46)	7.2–7.0[d]	6.0–5.8 m								
4e	C	2848	1600	$CDCl_3$	(3.41)	7.2–7.0[d]	5.9–5.7 m								
4f	B		1630 (1730)	$CDCl_3$	(2.52[e])	7.10	6.0–5.8 m								
4g	B	2838	1632	$CDCl_3$	(3.48)	7.03	5.96 t (6.0)	135.3	118.0	137.8	128.3 d (183.6)	193.5	319 (100)	320 (24.5)	319
4h	B	2840	1625	$CDCl_3$	(3.45)	6.75	5.97 t (6.0)								
4i	B	2842	1625	$CDCl_3$	(3.45)	6.72	5.76 t (5.6)								
4j	C	2852	1642	$CDCl_3$	(3.49)	6.89	5.88 t (6.4)								
4k	B	2842	1625	$CDCl_3$	(3.36)	6.68	5.49 t (7.1)								

4l	B	2830	1623	$CDCl_3$	(3.38)	6.69	5.5–5.3 m 5.1–5.0 m									
8		3320	1680	$CDCl_3$	8.30	6.85 d (3.0)	5.7–5.8 m	128.9	114.1	132.5	118.5 d (187.5)	168.3	259 (100)	260 (17.6)	259	

[a] $^3J_{HH}$ (in Hz) are given in parentheses. [b] All NH signals of compounds **3** (and **8**) are broad singlets (1 H) and all the NCH_3 signals of compounds **4** are sharp singlets (3 H). [c] All the signals given are singlets unless specified otherwise. Only $^1J_{CH}$ (in Hz) are given in parentheses. [d] Within the aromatic proton signals. [e] The chemical shift of the $NCOCH_3$ protons.

Table V. Selected Spectral Data of Indoles 10–12 of Tables II and III

	IR $\nu_{C=O}$,	^{1}H NMR, δ[a]		^{13}C NMR, δ[b]									MS, m/z (rel intensity)		
indole	cm^{-1}	NCH_3(H)	HC-2	C-2	C-3	C-3a	C-4	C-5	C-6	C-7	C-7a	C=O	M^+	M + 1	base peak
10a	1609	3.72	6.91	132.0 d (186.6)	120.1	124.6	118.2 d (160.3)	127.4	51.1 d (131.6)	49.0 d (131.6)	134.5	190.9			
10b	1602	3.61	6.79	129.9 d (187.6)	118.6	119.6	120.7 d (166.5)	134.2	39.4 d (125.9)	35.1 d (125.3)	136.8	191.1	367 (100)	368 (31.6)	367
10c	1645	(11.60[c])	6.92										353 (93.6)	354 (26.1)	105
10d	1625	3.63	7.5–7.1[d]												
11a	1610	3.76	8.16	138.4 d (183.5)	115.8	126.9	121.0 d (162.6)	139.1	129.3	125.8	134.2	190.7	351 (100)	352 (27.7)	351
11b	1628	3.94	7.99	139.8 d (184.6)	114.3	125.6	120.7 d (164.4)	138.0	128.3	121.3	135.4	190.1	365 (100)	366 (26.8)	365
11c	1615	3.91	8.00	140.6 d (183.8)	115.2	126.7	121.5 d (162.4)	137.9	135.5	126.9	137.8	190.1	379 (100)	380 (29.5)	379
11d	1612	3.91	8.03	140.5 d (183.9)	114.7	126.3	121.8 d (162.5)	138.4	135.3	124.8	135.2	190.3	393 (87.1)	394 (26.7)	105
11e	1615	3.92	8.00	140.7 d (188.3)	114.6	127.9	121.7 d (162.8)	139.0	135.9	124.8	135.0	190.2	449 (52.5)	450 (13.1)	105
11f	1628	4.02	8.12	138.8 d (182.0)	115.8	127.0	120.9 d (163.9)	137.4	137.3	125.4	135.0	192.2	317 (100)	318 (24.2)	318
11g	1680	4.12[c]	7.86	137.9 d (188.1)	104.4	124.7	118.9 d (161.2)	136.6	128.8	122.1	135.0	164.4	319 (76.0)	320 (14.8)	246
11h	1615	3.69	8.31	140.8 d (182.5)	115.0	128.7	118.7 d (161.8)	135.9	125.7 d (161.5)	121.6	135.5	190.4	325 (100)	326 (25.7)	325
11i	1590	(11.95[c])	8.31										351 (100)	352 (27.8)	351
11j	1640	4.43[c]	8.45	140.8 d (184.5)	115.9	122.9	120.5 d (162.7)	137.6	130.7	128.6	136.1	190.5	361 (100)	362 (30.7)	361
12a	1618	3.87	7.9–7.1[d]	137.3 d (183.5)	118.3	125.7	128.0	127.5	137.5	121.4	132.8	191.1	325 (100)	326 (26.0)	325
12b	1610	3.88	7.5–6.8[d]	136.8 d (184.6)	114.0	119.9	127.5	135.8	137.6	121.6	133.4	181.2	351 (100)	352 (25.3)	351
12c	1640	3.80	7.16	138.9 d (183.4)	113.4	122.1	145.7	111.5	132.2	122.1	134.0	188.7	343 (100)	344 (27.0)	343

[a] Given peaks are singlets or broad singlets in case of NH. [b] Given peaks are singlets, unless specified otherwise. The coupling constants (in Hz) are in parentheses. [c] $(CD_3)_2SO$ was used as a solvent for ^{1}H and ^{13}C NMR spectra. [d] Overlapping with the aromatic proton signals.

determination calcd for $C_{27}H_{25}NO_2$ 395.1884, found 395.1885.

3-Benzoyl-5-phenyl-5a,6,7,8,9,9a-hexahydro-1-methylbenz[*g*]indole (10b). 4-Benzoyl-2-cyclohex-1′-enyl-3-[(*E*)-2′-phenylethenyl]-1-methylpyrrole (**4c**, 1.83 g, 5 mmol) was dissolved in triglyme (20 mL). The solution was kept gently boiling for 1 h, then cooled to room temperature, and poured into 150 mL of cold water. The yellow precipitate was collected, washed with water (2 × 50 mL), and dried in vacuum to give 1.76 g (96%) of **10b** as yellow crystals (recrystallized from 1:1 CH_2Cl_2/*n*-pentane): mp 168–170 °C; IR 2905, 2840, 1602 (C=O, C=C), 1505, 1425, 1365, 1295, 905, 698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8 Hz, 2), 7.45–7.12 (m, 9), 6.79 (s, 1), 3.69–3.74 (m, 1), 3.61 (s, 3), 2.96–3.05 (m, 1), 1.81–2.02 (m, 2), 1.59–1.41 (m, 4), 1.32–1.19 (m, 2); ^{13}C NMR ($CDCl_3$) δ(benzoyl) 127.5 (d, C-2, C-6), 127.8 (d, C-3, C-5), 130.7 (d, C-4), 140.6 (s, C-1), δ(phenyl) 125.9 (d, C-4), 126.7 (d, C-2, C-6), 128.4 (d, C-3, C-5), 141.3 (s, C-1), δ(tetrahydrobenzo) 22.9 (t, *J* = 123.0 Hz, C-3), 23.7 (t, *J* = 123.0 Hz, C-2), 26.7 (t, *J* = 124.2 Hz, C-4), 26.9 (t, *J* = 124.8 Hz, C-1), δ(dihydroindole) 35.1 (d, *J* = 125.3 Hz, C-7), 39.4 (d, *J* = 125.9 Hz, C-6), 118.6 (s, C-3), 119.6 (s, C-3a), 120.7 (d, *J* = 166.5 Hz, C-4), 129.9 (d, *J* = 187.6 Hz, C-2), 134.2 (s, C-5), 136.8 (s, C-7a), δ 34.6 (q, *J* = 139.1 Hz, NCH_3), 191.1 (s, C=O); mass spectrum, *m/z* (relative intensity) 367 (M^+, 100), 368 (31.6), 365 (10.4), 324 (12.8), 240 (8.9), 234 (11.4), 124 (11.1), 105 (71.8), 77 (19.2). Anal. Calcd for $C_{26}H_{25}NO$ (367.20): C, 85.00; H, 6.86; N, 3.81. Found: C, 84.85; H, 6.88; N, 3.76.

3-Benzoyl-5a,6,7,8,9,9a-hexahydro-5-phenylbenz[*g*]indole (10c). A solution of 4-benzoyl-2-(cyclohex-1′-enyl)-3-[(*E*)-2′-phenylethenyl]pyrrole (**3i**, 0.35 g, 1.0 mmol) in triglyme (10 mL) was gently refluxed for 1 h and then poured into 100 mL of cold water. The yellow precipitate was collected, washed with water, and dried in vacuum to give 0.33 g (94%) of **10c** as yellow crystals (EtOH): mp 251–254 °C; IR 3280 (NH), 2920, 1645 (C=O), 1510, 1420, 1365, 1262, 1218, 900 cm^{-1}; ^1H NMR [$(CD_3)_2SO$] δ 11.60 (s, 1, NH), 7.8–6.9 (m, 12), 3.1–2.9 (m, 2), 1.7–1.2 (m, 6); mass spectrum, *m/z* (relative intensity): 353 (M^+, 93.6), 354 (26.1), 351 (19.1), 310 (17.7), 276 (10.1), 220 (12.0), 165 (4.7), 116 (11.7), 105 (100), 77 (32.1), 28 (17.3). Anal. Calcd for $C_{25}H_{23}NO$ (353.18): C, 84.94; H, 6.56; N, 3.96. Found: C, 84.99; H, 6.52; N, 3.57.

3-Benzoyl-6,7-dihydro-1,7-dimethyl-5-phenylindole (10d) and 3-Benzoyl-4,5-dihydro-1,7-dimethyl-5-phenylindole. A solution of 4-benzoyl-1-methyl-3-[(*E*)-2′-phenylethenyl]-2-prop-2′-enylpyrrole (**4l**, 1.64 g, 5.0 mmol) in dry cyclohexane (120 mL) containing 2% EtOH was irradiated with a high-pressure immersion mercury UV lamp (HANAU TQ 150) at room temperature for 12 h. The solution was concentrated and a solid residue (1.50 g, 90%) was purified by crystallization from CH_2Cl_2/*n*-pentane (1:1). The yellow crystals (1.45 g, 87%) appeared to be a 1:1 mixture of **10d** and its 4,5-dihydro isomer. Attempts to separate these isomers by chromatography or crystallization were unsuccessful: mp 75–79 °C; IR 2960, 2930, 1625 (C=O), 1505, 1440, 1370, 1260, 1218, 940 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.6 (m, 2), 7.5–7.1 (m, 11), 5.6–5.4, 4.95 (m, d, *J* = 8.1 Hz, 1), 3.63 and 3.46 (2 s, 3), 3.3–2.5 (m, 3), 2.16, 1.21, and 1.12 (s and 2 d, *J* = 5.9 Hhz, 3). Anal. of mixture of isomers calcd for $C_{23}H_{21}NO$ (327.16): C, 84.36; H, 6.45; N, 4.28; found: C, 84.18; H, 6.40; N, 4.15.

3-Benzoyl-7,8-dihydro-1-methyl-5-phenyl-6*H*-cyclopent[*g*]indole (11a). A solution of 4-benzoyl-2-cyclopent-1′-enyl-3-[(*E*)-2′-phenylethenyl]-1-methylpyrrole (**4a**, 1.76 g, 5.0 mmol) in dry triglyme (20 mL) was gently refluxed for 1 h. The yellow-orange solution was cooled to approximately 80 °C, and DDQ (1.18 g, 5.2 mmol) was added. The dark red mixture was stirred at 80 °C for 30 min and then poured into 200 mL of cold water. The mixture was stirred for 30 min. The precipitate (2 g) was collected, washed several times with cold water, and dried in air. Purification was performed over alumina (Brockmann 90, II/III, 200 g; 8:1 CH_2Cl_2/*n*-pentane) to give 1.46 g (83%) of **11a** as colorless prisms, which were recrystallized from EtOH: mp 172–173 °C; IR 3050, 2940, 2840, 1610 (C=O), 1520, 1450, 1440, 1362, 1225, 1140, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.16 (s, 1), 7.6–7.4 (m, 2), 7.3–7.0 (m, 9), 3.76 (s, 3), 3.21 (t, *J* = 4.2 Hz, 2), 2.89 (t, *J* = 4.2 Hz, 2), 2.01 (quint, *J* = 4.2 Hz, 2); ^{13}C NMR ($CDCl_3$) δ(benzoyl) 128.4 (d, C-2, C-6, C-3, C-5), 130.7 (d, C-4), 140.9 (s, C-1); δ(cyclopenta) 25.6 (t, *J* = 125.4 Hz, C-2), 33 (t, *J* = 126.8 Hz, C-3), 32.6 (t, *J* = 127.0 Hz, C-1), δ(dihydroindole) 115.8 (s, C-3), 121.0 (d, *J* = 162.6 Hz, C-4), 125.8 (s, C-7), 126.9 (s, C-3a), 129.3 (s, C-6), 134.2 (s, C-7a), 138.4 (d, *J* = 183.5 Hz, C-2), 139.1 (s, C-5) δ(phenyl) 126.3 (d, C-4), 127.9 (d, C-2, C-6), 128.8 (d, C-3, C-5), 142.1 (s, C-1), δ 35.8 (q, *J* = 139.3 Hz, NCH_3), 190.7 (s, C=O); mass spectrum, *m/z* (relative intensity) 351 (M^+, 100), 352 (27.7), 349 (12.7), 274 (40.0), 244 (6.8), 202 (2.9), 161 (3.0), 105 (16.6), 77 (8.2), 28 (13.0). Anal. Calcd for $C_{25}H_{21}NO$ (351.16): C, 85.43; H, 6.03; N, 3.99. Found: C, 84.86; H, 5.91; N, 3.99.

3-Benzoyl-1,7-dimethyl-5-phenylindole (11h). A mixture of 4-benzoyl-6,7-dihydro-1,7-dimethyl-5-phenylpyrrole (**10d**) and isomeric 4-benzoyl-4,5-dihydro-1,7-dimethyl-5-phenylpyrrole (1.0 g, 3.1 mmol) in 25 mL of dry benzene was gently refluxed with 0.80 g of DDQ (3.5 mmol) for 30 min. The mixture was cooled to room temperature and filtered over alumina (Brockmann 90, II/III; 45 g). The yellow filtrate was concentrated, and the crystalline residue (0.95 g, 95%) was purified by crystallization from EtOH to give 0.9 g (90%) of **11h** as colorless crystals: mp 164–165 °C; IR 3050, 3030, 2930, 1615 (C=O), 1522, 1455, 1365, 1295, 1230, 1100, 915 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.31 (s, 1), 7.6–6.9 (m, 12), 3.69 (s, 3), 2.50 (s, 3); ^{13}C NMR ($CDCl_3$) δ(benzoyl) 128.4 (d, C-2, C-6, C-3, C-5), 130.8 (d, C-4), 139.8 (s, C-1), δ(indole) 115.0 (s, C-3), 118.7 (d, *J* = 161.8 Hz, C-4), 121.6 (s, C-7), 125.7 (d, *J* = 161.5 Hz, C-6), 128.7 (s, C-3a), 135.5 (s, C-7a), 135.9 (s, C-5), 140.8 (d, *J* = 182.5 Hz, C-2), δ(phenyl) 126.5 (d, C-4), 127.2 (d, C-2, C-6), 128.1 (d, C-3, C-5), 141.4 (s, C-1), δ 19.4 (q, *J* = 124.1 Hz, CH_3), 37.4 (q, *J* = 137.2 Hz, NCH_3), 190.4 (s, C=O); mass spectrum, *m/z* (relative intensity) 325 (M^+, 100), 326 (25.7), 249 (16.5), 248 (83.4), 218 (3.9), 204 (10.6), 178 (8.0), 105 (4.4), 77 (15.2). Anal. Calcd for $C_{23}H_{19}NO$ (325.15): C, 84.88; H, 5.89; N, 4.31. Found: C, 84.50; H, 5.82; N, 4.31.

3-Benzoyl-5-phenyl-6,7,8,9-tetrahydrobenz[*g*]indole (11i) and 2-Acetyl-3-benzoyl-5-phenyl-6,7,8,9-tetrahydrobenz[*g*]indole. A solution of 1-acetyl-2-cyclohex-1′-enyl-3-[(*E*)-2′-phenylethenyl]pyrrole (**4f**, 2.3 g, 5.8 mmol) was gently refluxed for 1 h. The mixture was cooled to 80 °C and DDQ (1.35 g, 5.9 mmol) was added. the mixture was stirred at 80°C for 30 min, then poured into 200 mL of cold water, and, next, stirred for another 30 min. The black precipitate (2.2 g) was collected, washed with cold water, and dried in air. It was purified on a column of alumina (Brockmann 90, II/III, 200 g; 8:1 CH_2Cl_2/*n*-pentane) to give 1.8 g (79%) of yellowish crystals, which formed a mixture of **11i** and 2-acetyl-3-benzoyl-5-phenyl-6,7,8,9-tetrahydrobenz[*g*]indole. The components were separated by column chromatography (Al_2O_3, Brockmann 90, II/III, 500 g; eluent, 5:1 CH_2Cl_2/*n*-pentane) to give 0.6 g (31%) of **11i** as white prisms; mp 233–234 °C, and 1.1 g (48%) of pale yellow prisms of the 2-acetyl derivative, mp 207–208 °C. Compound **11i**: IR 3200 (NH) 3030, 2910, 1590 (C=O), 1558, 1510, 1430, 1190, 1160, 1125, 880 cm^{-1}; ^1H NMR [$(CD_3)_2SO$] δ 11.95 (s, 1, NH), 8.31 (s, 1), 8.05 (s, 1), 7.9–7.4 (m, 10), 3.2–2.8 (m, 2), 2.7–2.4 (m, 2), 1.9–1.6 (m, 4); mass spectrum, *m/z* (relative intensity) 351 (M^+, 100), 352 (27.8), 349 (12.7), 347 (91.2), 323 (9.5) 274 (25.2), 270 (42.6), 241 (9.2), 211 (21.9), 134 (11.8), 105 (52.5), 77 (42.5). Anal. Calcd for $C_{25}H_{21}NO$ (351.16): C, 85.43; H, 6.02; N, 3.99. Found: C, 85.38; H, 6.13; N, 3.89. 2-Acetyl-3-benzoyl-5-phenyl-6,7,8,9-tetrahydrobenz[*g*]indole: IR 3320 (NH), 3080, 2930, 1655 (MeC=O), 1630 (C=O), 1518, 1410, 1362, 1270, 1228, 1218, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.5–9.2 (m, 1), 8.0–7.8 (m, 2), 7.6–7.1 (m, 4), 7.22 (s, 5), 6.95 (s, 1), 3.1–2.8 (m, 2), 2.7–2.4 (m, 2), 2.41 (s, 3), 1.9–1.6 (m, 4); ^{13}C NMR ($CDCl_3$) δ(benzoyl) 128.5 (d, C-2, C-6), 129.3 (d, C-3, C-5), 133.5 (d, C-4), 141.8 (s, C-1), δ(phenyl) 126.5 (d, C-4), 127.8 (d, C-2, C-6), 130.0 (d, C-3, C-5), 138.3 (s, C-1), δ(tetrahydrobenzo) 21.9 (t, *J* = 124.6 Hz, C-3), 23.1 (t, *J* = 125.0 Hz, C-2), 24.4 (t, *J* = 125.9 Hz, C-4), 28.7 (t, *J* = 127.3 Hz, C-1), δ(indole) 120.1 (d, *J* = 161.5 Hz, C-4), 120.5 (s, C-3), 121.3 (s, C-7), 124.5 (s, C-3a), 128.3 (s, C-6), 133.8 (s, C-2), 134.1 (s, C-7a), 137.7 (s, C-5), δ 28.3 (q, *J* = 127.3 Hz, CH_3), 190.9 (s, PhC=O), 193.7 (s, MeC=O); mass spectrum, *m/z* (relative intensity) 393 (M^+, 100), 394 (30.0), 316 (17.3), 274 (4.4), 105 (39.9), 77 (51.0), 51 (7.5), 43 (37.0), 28 (7.9). Anal. Calcd for $C_{27}H_{23}NO_2$ (393.17): C, 82.41; H, 5.90; N, 3.56. Found: C, 82.31; H, 5.96; N, 3.52.

3-Benzoyl-1-methyl-5-phenylbenz[*g*]indole (11j). A mixture of 3-benzoyl-1-methyl-5-phenyl-6,7,8,9-tetrahydrobenz[*g*]indole (**11b**, 0.5 g, 1.4 mmol) and DDQ (0.68 g, 3.0 mmol) in diglyme [bis(2-methoxyethyl) ether, 30 mL] was stirred at 80 °C for 1 h and then poured into 100 mL of cold water. The precipitate (0.52

g) was collected, washed with cold water, and dried in air. Chromatography over alumina (Brockmann 90, II/III; eluent, CH_2Cl_2) gave 0.49 g (98%) of **11j** as white needles: mp 238–239 °C (EtOH); IR 3045, 1640 (C=O), 1625, 1600, 1530, 1442, 1405, 1356, 1230, 915 cm^{-1}; ^1H NMR [$(CD_3)_2SO$] δ 8.45 (s, 1), 8.08 (s, 1), 8.0–7.6 (m, 9), 7.62 (s, 5), 4.43 (s, 3); ^{13}C NMR [$(CD_3)_2SO$] δ(benzoyl) 128.5 (d, C-2, C-6), 128.7 (d, C-3, C-5), 131.1 (d, C-4), 141.4 (s, C-1), δ(phenyl) 126.9 (d, C-4), 128.2 (d, C-2, C-6), 130.4 (d, C-3, C-5), 137.7 (s, C-1), δ(benzo) 122.3 (d, C-3), 124.1 (s, C-2), 127.8 (d, C-4), 128.0 (d, C-1), δ(indole) 115.9 (s, C-3), 120.5 (d, J = 162.7 Hz, C-4), 122.9 (s, C-3a), 128.6 (s, C-7), 130.7 (s, C-6), 136.1 (s, C-7a), 137.6 (s, C-5), 140.8 (d, J = 184.5 Hz, C-2), δ 39.4 (q, J = 139.2 Hz, NCH_3), 190.5 (s, C=O); mass spectrum, m/z (relative intensity) 361 (M^+, 100), 362 (30.7), 284 (30.9), 253 (3.8), 229 (2.9), 180 (2.9), 141 (20.6), 105 (7.8), 77 (8.2), 28 (3.4). Anal. Calcd for $C_{26}H_{19}NO \cdot H_2O$ (379.17): C, 82.29; H, 5.58; N, 3.69. Found: C, 82.63; H, 5.31; N, 3.64.

3-Benzoyl-9,10-dihydro-1-methyl-8*H*-benzo[*e*]cyclopent-[*g*]indole (12a). 3-Benzoyl-2-cyclopent-1′-enyl-1-methyl-3-phenylpyrrole (**4b**, 0.90 g, 4.1 mmol) was dissolved in MeOH (30 mL), and this solution was diluted with 70 mL of dry cyclohexane. The stirred mixture was irradiated with a high-pressure immersion mercury UV lamp (HANAU TQ 150) at room temperature for 12 h. The solvent was removed and the crystalline residue (0.73 g) containing approximately 70% of **12a** and 30% of its 6,7-dihydro derivative (by ^1H NMR) was dissolved in 20 mL dry benzene. The solution was gently refluxed for 30 min with DDQ (0.40 g, 1.8 mmol) and, after cooling to room temperature, filtered over alumina (Brockmann 90, II/III). Crude **12a** was purified by crystallization from CH_2Cl_2/*n*-pentane (1:2) to give 0.68 g (76%) of yellow crystals: mp 148–149 °C; IR 1618 (C=O), 1605, 1595, 1520, 1400, 1358, 1060, 1030, 815, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.3–9.1 (m, 1), 7.9–7.7 (m, 3), 7.5–7.0 (m, 6), 3.87 (s, 3), 3.5–3.1 (m, 4), 2.4–2.0 (m, 2); ^{13}C NMR ($CDCl_3$) δ(benzoyl) 127.9 (d, C-3, C-5), 129.3 (d, C-2, C-6), 131.2 (d, C-3), 141.2 (s, C-1), δ(cyclopenta) 23.8 (t, J = 130.2 Hz, C-2), 30.9 (t, J = 130.7 Hz, C-3), 32.3 (t, J = 130.7 Hz, C-1), δ(benzo) 124.1 (d, J = 159.8 Hz, C-4), 124.4 (d, J = 159.8 Hz, C-2), 124.6 (d, J = 159.8 Hz, C-3), 126.8 (d, J = 159.8 Hz, C-1), δ(indole) 118.3 (s, C-3), 121.4 (s, C-7), 125.7 (s, C-3a), 127.5 (s, C-5), 128.0 (s, C-4), 132.8 (s, C-7a), 137.3 (d, J = 183.5 Hz, C-2), 137.5 (s, C-6), δ 36.0 (q, J = 139.1 Hz, NCH_3), 191.1 (s, C=O); mass spectrum; exact mass calcd for $C_{23}H_{19}NO$ 325.1466, found 325.1476; mass spectrum m/z (relative intensity) 325 (M^+, 100), 326 (26.0), 323 (7.3), 298 (30.7), 248 (26.5), 220 (4.5), 208 (5.9), 194 (5.9), 105 (23.4) 84 (7.0), 77 (14.2), 28 (2.5). Anal. Calcd for $C_{23}H_{19}NO$ (325.15): C, 84.88; H, 5.89; N, 4.31. Found: C, 84.96; H, 6.00; N, 4.42.

1-Methyl-7,8,9,10-tetrahydro-3-(2′-thenoyl)benzo[*g*]-thieno[2,3-*e*]indole (12b). 2-Cyclohex-1′-enyl-1-methyl-4-(2′-thenoyl)-3-(2′-thienyl)pyrrole (**4e**, 1.0 g, 2.8 mmol) was dissolved in 150 mL of cyclohexane containing 3% ethanol. This solution was irradiated as described for **12a**. Then the reaction mixture was concentrated, and the crude dihydro derivative of **12b** (0.92 g; exact mass calcd 353.092, found 353.091) was dissolved in 80 mL of benzene and was gently refluxed for 30 min with DDQ (0.70 g, 3.1 mmol). Benzene was removed, and the black residue was dissolved in CH_2Cl_2 (3 mL) and purified on a short column of alumina (Brockmann 90, II/III, 20 g; eluent, 8:1 CH_2Cl_2/*n*-pentane) to give 0.9 g of yellow crystals which were further purified by crystallization from CH_2Cl_2/*n*-pentane (1:2) to yield 0.8 g (78%) of **12b**: mp 205–206 °C; IR 2935, 1610 (C=O), 1595, 1530, 1445, 1355, 1255, 810, 780, 725, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5–6.8 (m, 6), 3.88 (s, 3), 3.1–2.8 (m, 4), 1.9–2.8 (m, 4); ^{13}C NMR ($CDCl_3$) δ(tetrahydrobenzo) 25.8 (t, J = 126.2 Hz, C-2), 26.0 (t, J = 126.2 Hz, C-3), 27.7 (t, J = 127.0 Hz, C-4), 28.7 (t, J = 127.0 Hz, C-1), δ(thieno) 123.3 (d, J = 189.3 Hz, C-1), 130.5 (d, J = 165.8 Hz, C-2), δ(thenoyl) 127.2 (d, J = 166.2 Hz, C-3), 131.2 (d, J = 188.9 Hz, C-4), 131.5 (d, J = 175.3 Hz, C-2), 145.1 (s, C-1), δ(indole) 114.0 (s, C-3), 119.9 (s, C-3a), 121.6 (s, C-7), 127.5 (s, C-4), 133.4 (s, C-7a), 135.8 (s, C-5), 136.8 (d, J = 184.6 Hz, C-2), 137.6 (s, C-6), δ 38.5 (q, J = 138.7 Hz, NCH_3), 181.2 (s, C=O); mass spectrum, exact mass calcd for $C_{20}H_{17}NOS_2$ 351.0751, found 351.0759; mass spectrum, m/z (relative intensity) 351 (M^+, 100), 352 (25.3), 353 (42.7), 323 (16.4), 310 (15.8), 240 (6.5), 113 (6.5), 111 (38.7), 28 (5.9). Anal. Calcd for $C_{19}H_{17}NOS_2$: C, 68.36; H, 4.88; N, 3.99; S, 18.21. Found: C, 68.44; H, 4.90; N, 4.08; S, 18.33.

3-Benzoyl-1-methyl-8,9,10,11-tetrahydro-7*H*-cyclohepta-[*g*]furo[2,3-*e*]indole (12c). 4-Benzoyl-2-cyclohept-1′-enyl-3-(2′-furyl)-1-methylpyrrole (**4j**, 0.9 g, 2.6 mmol) was dissolved in 150 mL of cyclohexane containing 5% EtOH. This solution was irradiated as described for **12a**. The reaction mixture was concentrated to give the yellow crystalline dihydro derivative of **12c** (0.8 g; mp 74–75 °C; exact mass calcd for $C_{23}H_{23}NO_2$ 345.173, found 345.174). This material was gently refluxed for 30 min with DDQ (0.65 g, 2.8 mmol) in 80 mL of benzene. Benzene was removed, and the black residue was dissolved in CH_2Cl_2 (3 mL) and purified on a column of alumina (Brockmann 90, II/III; eluent, 8:1 CH_2Cl_2/*n*-pentane) to give 0.65 g (73%) yellow crystals of **12c**: mp 207–209 °C; IR 2920, 2845, 1640 (C=O), 1525, 1450, 1400, 1348, 1255, 1205, 1145, 1075, 865, 735, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.84 (d, J = 1.8 Hz, 1), 7.72 (d, J = 3.2 Hz, 1), 7.58 (d, J = 2.1 Hz, 1), 7.4–7.2 (m, 3), 7.16 (s, 1), 6.75 (d, J = 2.1 Hz, 1), 3.80 (s, 3), 3.3–2.9 (m, 4), 1.9–1.5 (m, 6); ^{13}C NMR ($CDCl_3$) δ(benzoyl) 127.6 (d, C-3, C-5), 128.7 (d, C-2, C-6), 130.7 (d, C-3), 140.1 (s, C-1), δ(cyclohepta) 26.9 (t, J = 124.9 Hz, C-2, C-3, C-4), 30.5 (t, J = 124.0 Hz, C-5), 31.3 (t, J = 124.0, C-1), δ(furo) 105.0 (d, J = 172.2 Hz, C-2), 142.5 (d, J = 202.9 Hz, C-1), δ(indole) 111.5 (s, C-5), 113.4 (s, C-3), 122.1 (s, C-3a, C-7), 132.2 (s, C-6), 134.0 (s, C-7a), 138.9 (d, J = 183.4 Hz, C-2), 145.7 (s, C-4), δ 38.8 (q, J = 140.5 Hz, NCH_3), 188.7 (s, C=O); mass spectrum; exact mass calcd for $C_{23}H_{21}NO_2$ 343.1571, found 343.1564; mass spectrum, m/z (relative intensity) 343 (M^+, 100), 344 (27.0), 314 (15.3), 288 (17.8), 266 (17.8), 110 (77.7), 105 (27.1), 77 (23.9), 28 (16.6). Anal. Calcd for $C_{23}H_{21}NO_2$ (343.16): C, 80.43; H, 6.17; N, 4.08. Found: C, 80.82; H, 6.23; N, 4.12..

Supplementary Material Available: Complete spectral data (^1H and ^{13}C NMR, mass, and IR) and combustion microanalyses of the pyrroles (Table I) and indoles (Tables II and III) (17 pages). Ordering information is given on any current masthead page.