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Indolenine Oxides, IX[1]

Novel Polycyclic Linearly Conjugated Cyclohexadiene Imines from Rearrangement of Unstable Tetrahydroisoxazolo[2,3-*a*]-indoles[2a,b]

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From 1,3-dipolar cycloaddition of the symmetrically substituted olefins **2a – e** to the sterically overcrowded nitrone **6**, the primary cycloadducts, i.e. the 2,3,3a,4-tetrahydroisoxazolo[2,3-*a*]-indoles **7a – e**, are obtained only by direct crystallization from the chilled reaction mixtures in the absence of acid. Upon storage of the solutions at room temperature, especially in the presence of catalytic quantities of acid, or during chromatography on silica gel, **7a, c – e** undergo rearrangement to the cyclohexadiene imines **8a, c – e**. The latter in turn are of limited stability in solution and are transformed into indolines or derivatives of 3*H*-indole under partial removal of the epoxyethano bridge. The structure of **8a** has unambiguously been proven by X-ray crystallography. – The analogous primary cycloadducts **3a – d** of the sterically non crowded nitrone **1** are stable and – with one exception in very low yield – do not undergo the rearrangement reported for **7a, c – e**.

Indoleninoxide, IX[1]

Neuartige polycyclische linear konjugierte Cyclohexadienimine durch Umlagerung instabiler Tetrahydroisoxazolo[2,3-*a*]indole[2a,b]

Bei der 1,3-dipolaren Cycloaddition der symmetrisch substituierten Olefine **2a – e** an das sterisch überbeanspruchte Nitron **6** werden die primären Cycloaddukte, die 2,3,3a,4-Tetrahydroisoxazolo[2,3-*a*]indole **7a – e** nur erhalten, wenn sie in Abwesenheit von Säure aus den gekühlten Reaktionsansätzen direkt auskristallisieren. Beim Aufbewahren der Lösungen bei Raumtemperatur, insbesondere bei Anwesenheit katalytischer Mengen Säure, oder bei der Chromatographie an Kieselgel wandeln sich **7a, c – e** in die Cyclohexadienimine **8a, c – e** um. Letztere sind in Lösung ebenfalls nur begrenzt haltbar und gehen teilweise unter Abbau der Epoxyethanobrücke in Indolin- oder 3*H*-Indolderivate über. Die Konstitution von **8a** wurde durch Röntgenstrukturanalyse bewiesen. – Die analogen primären Cycloaddukte **3a – d** des sterisch nicht überbeanspruchten Nitrons **1** sind stabil und zeigen – mit einer in sehr niedriger Ausbeute verlaufenden Ausnahme – die für **7a, c – e** beschriebene Umlagerung nicht.

1,3-Dipolar cycloadditions of nitrones are well known[3]. Therefore, the easily accessible 3*H*-indole 1-oxides **1**[4a] and **6**[4b] were subjected to cycloaddition to a variety of dipolarophiles[2]

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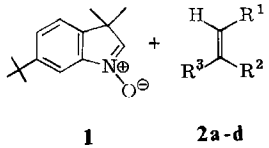
with the aim of obtaining information about the general reactivity of **1** and **6**. From the He-I_α-photoelectron spectra[5], lowest ionization potentials of −8.14 eV for **1** and −7.9 eV for **6** could be extracted. These values fall into the range of first ionization potentials reported for other nitrones[6] and allow – together with the fact that **1** and **6**, being *cis*-fixated aldonitrones, show little hindrance to additions at the α-carbon atom – to expect smooth cycloadditions of electron poor alkenes.

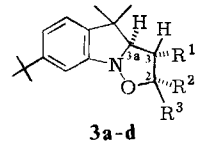
Special emphasis had been laid on the question whether steric overcrowding in **6** had any noticeable effect on rates and/or product distribution. In cycloadditions of unsymmetrically substituted (both electron poor and electron rich) alkenes the bulky 7-*tert*-butyl group in **6** had no effect on the direction of addition, but it always destabilized the adducts[7]. A destabilization effect is also to be anticipated in this study on the cycloaddition of maleic and fumaric acid derivatives to **6** in comparison with the corresponding additions to **1**.

Results

Cycloaddition of dimethyl fumarate (**2a**), dimethyl maleate (**2b**), *N*-phenylmaleic imide (**2c**), and fumarodinitrile (**2d**) to **1** in benzene solution at ambient temperature or with gentle warming gave the primary adducts **3a–d** in good yields. Except for the addition of **2c**, which gave 21% **4** in addition to 70% of **3c**, the other *a priori* possible diastereomer was shown to be either completely absent or formed in at best 3% yield by careful chromatographic work-up. The *syn* adduct **4** may be transformed quantitatively into **3c** by refluxing a xylene solution of **4** for a few hours under a nitrogen atmosphere.

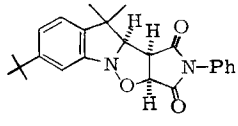


1 **2a-d**

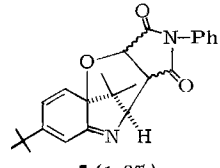


3a-d

3	%
a	90
b	85
c	70
d	79



4 (21%)



5 (1.8%)

2, 3, 7, 8	R^1	R^2	R^3
a	CO_2CH_3	H	CO_2CH_3
b	CO_2CH_3	CO_2CH_3	H
c	–CO–N(Ph)–CO–		H
d	CN	H	CN
e	CN	CN	H

Another by-product, isomeric to **3c**, emanated from the cycloaddition of **2c** to **1** in low yield (<2%), decomposing upon prolonged storage. Structure **5** was assigned on the basis of the findings with compound **6** reported below and the following spectral data: Whereas all signals attributable to eight aryl protons in the ^1H NMR spectrum of compounds **3c**, **4** fall into the range of δ = 6.97 to 7.61 (in $CDCl_3$), compound **5** exhibits only a multiplet attributable to five aryl hydrogens, but in the range of δ = 5.9 to 6.7 an AB-quartet (δ_A = 6.55, δ_B = 6.07, J = 10 Hz) perturbed by a third proton (δ = 6.25) interacting with approximate coupling constants of 1.4 and 1.0 Hz, respectively, appeared and was assigned to the cyclohexadienoid system. Further, the methyl signals of **5** are shifted upfield (δ = 0.87 and 1.38) compared to **3c** and **4** (see table 1).

Table 1. ^{1}H NMR data of 2,3,3a,4-tetrahydroisoxazolo[2,3-*a*]indoles

compd.	m.p. [°C]	solvent	δ [ppm] (multiplicity) 2-H (d)	3-H (dd)	3a-H (d)	^3J [Hz] 2,3	3,3a
3b	135	$CDCl_3$	4.67	3.43	4.17	9.3	8.1
3a	115	$CDCl_3$	4.95	3.74[a]	4.06	5.7	7.5
		C_6D_6	5.10	3.98	4.18	5.7	7.5
3c	206 – 208	$CDCl_3$	4.78	3.70	4.06	8.1	5.4
		C_6D_6	4.25	2.85	3.86	8.1	5.4
4	120 – 121	$CDCl_3$	5.11	3.73	4.08	7.8	8.1
		C_6D_6	4.51	2.90	3.51	7.8	8.1
3d	125[b]	$CDCl_3$	5.00	3.49	4.00	6.0	7.8
7a	106	$CDCl_3$	5.05	3.8[c]	4.10	7.6	4.0
		C_6D_6	5.36	4.04	4.31	7.6	4.0
7b	88	$CDCl_3$	4.67	3.60	4.27	8.6	6.6
7c	115[b]	$CDCl_3$	4.90	3.77	3.91	7.0	[d]
7d[e]	[d]	$CDCl_3$	5.00	3.77	4.10	7.0	4.8

compd.	Aryl	δ [ppm] (multiplicity, integral) 4-$(CH_3)_2$ (s)	$C(CH_3)_3$ (s)	OCH_3 (s)
3b	7.1 (m, 3)	1.33; 1.40	1.30	3.70; 3.77
3a		1.27; 1.47	1.27	3.52; 3.74
	6.8 – 7.45 (m, 3)	1.29; 1.38	1.29	3.15; 3.27
3c	6.97 – 7.61 (m, 8)	1.38; 1.62	1.33	
	7.13 (mc, 8)	1.13; 1.39	1.19	
4	6.48 (2), 7.28 (m, 6)	1.38; 1.85	1.13	
	6.92 (mc, 8)	1.26; 1.81	1.01	
3d	7.14 (m, 3)	1.37; 1.56	1.28	
7a	7.16 (d); 7.33 (d)	1.33 (m, 6)	1.33; 1.50	3.70; 3.80
	7.12 (d); 7.54 (d)	1.20; 1.37	1.31; 1.72	3.24; 3.33
7b	7.00 (d); 7.37 (d)	1.33; 1.40	1.33; 1.48	3.77; 3.82
7c	6.97 (d); 7.23 (d)	1.37 (m, 6)	1.33; 1.45	
	7.06 (m, 5, NPh)			
7d[e]	7.00 (d); 7.30 (d)	[d]	[d]	

[a] Perturbed by overlying singlet at δ = 3.74 (OCH_3). – [b] With decomposition. – [c] Poorly resolved. – [d] Not determined. – [e] Not isolated.

The structure of **3a** has been proven unambiguously by X-ray crystallographic analysis[8] (see fig. 1), which also removed ambiguities in structural assignments solely on the basis of proton-proton coupling constants.

A completely analogous structure was assigned to **3d** on the basis of close similarity of the values for $^3J_{2,3}$ and $^3J_{3,3a}$ for both compounds (see table 1). Whereas the considerably larger value (8.1 Hz) for $^3J_{3,3a}$ in **4** compared to 5.4 Hz in **3c** supports the assigned *syn*-structure for **4**, the difference in $^3J_{3,3a}$ values for **3a** (7.5 Hz) and **3b** (8.1 Hz) is too small to serve as a basis to assign a *syn*-structure also to the maleate adduct **3b**. By inspection of models, however, one may draw the conclusion that a *syn*-structure for **3b** would be highly hindered and unstable, thus the *anti*-structure **3b** is maintained.

Whereas the isoxazolidines **3a – d, 4** were the main products from cycloaddition of **1** to **2a – d** and proved to be stable towards recrystallization from various boiling

solvents, additions of **2a – e** to the sterically crowded nitrone **6** gave a more complex picture.

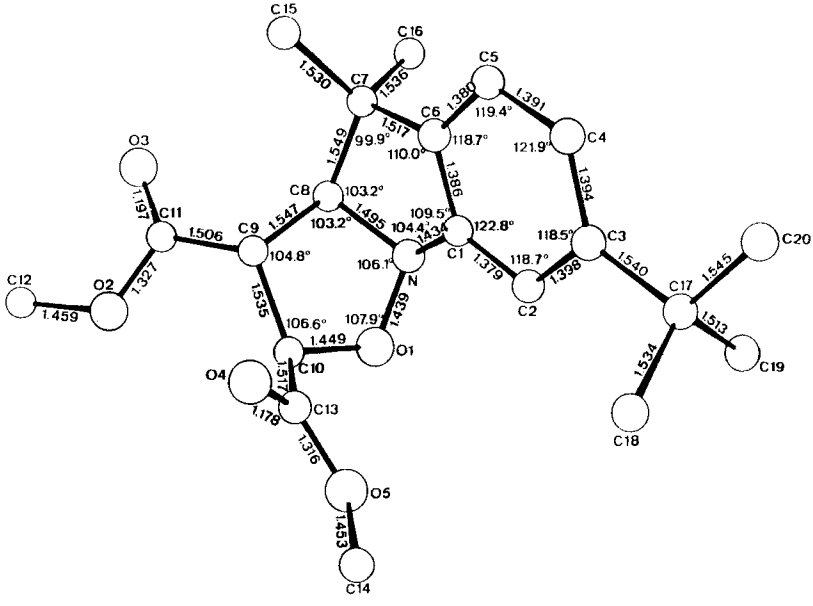
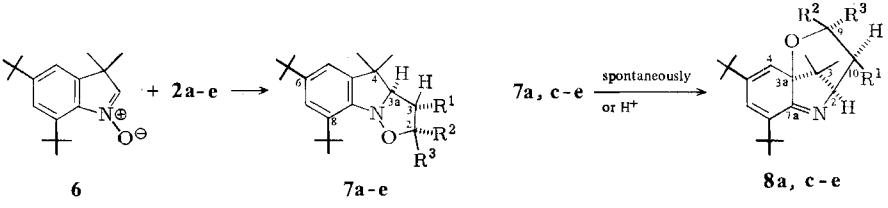
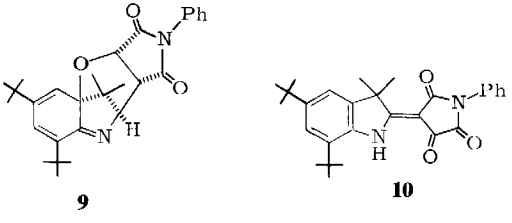


Figure 1. Molecular structure[8] of **3a** in the crystal. The numbering in the drawing is not that of systematic numbering





(mixture of *E*- and *Z*-isomers)

7a could be obtained from **2a** and **6** after allowing to react within 24 h at 0°C (and work-up at the same temperature) in 74% yield. A sample of **7a** left standing in $CDCl_3$ solution for two days at room temperature quantitatively rearranged to a non-aromatic product, the same result could be reached after one hour upon treatment of the sample

solution with one crystal of *p*-toluenesulfonic acid. Structure **8a** for the new product may be derived from its NMR spectral data (tables 2 and 3) but was rigorously proven by X-ray structural analysis (figure 2, table 4).

Table 2. ^{1}H NMR data of cyclohexadiene imines **8a,c–e** and **9** (δ, TMS = 0 ppm, $CDCl_3$)

compd.	m.p. [°C]	4-H/6-H (*J* [Hz])	3-$(CH_3)_2$	2-H (d)	10-H (dd)	9-H (d)
8a	200	5.73; 6.50 (1.6)	0.73; 1.27	4.42	3.30	4.40
8c	220–222	5.73; 6.70 (1.6)	0.82; 1.35	4.57	3.50	4.73
8d	181	5.67; 6.60 (1.6)	0.80; 1.30	4.50	3.50	4.37
8e	184–185	5.63; 6.70 (1.6)	0.80; 1.23	4.35	3.73	5.17
9	208	5.70; 6.60 (1.6)	0.78; 1.27	4.67	3.33	4.45

compd.	^3J [Hz] 2,10	9,10	*tert*-Bu (s)	other
8a	2.0	10.2	1.15; 1.37	OCH_3: 3.76 (6H)
8c	3.6	9.0	1.13; 1.37	NPh: 7.33 (m, 5H)
8d	1.6	10.4	1.17; 1.42	
8e	2.0	8.8	1.13; 1.47	
9	3.4	7.2	1.13; 1.38	NPh: 7.43 (m, 5H)

Table 3. ^{13}C NMR data of cyclohexadiene imines **8a,c,d** (δ, TMS = 0 ppm, $CDCl_3$)

assignment	multiplicity[a]	**8a**	**8c**	**8d**
3-(CH_3)$_2$	q	17.26; 23.84	17.81; 23.26	17.66; 23.52
C(CH_3)$_3$	q	28.77; 29.48	28.70; 29.63	28.62; 29.39
C(CH_3)$_3$	s	34.82; 35.39	31.70; 35.08	34.98; 35.57
C-2	d	70.91	69.10	61.20
C-3	s	50.24	48.80	49.70
C-3a	s	83.58	83.15	84.99
C-4	d	117.11	116.71	115.74
C-5	s	141.32	141.59	141.16
C-6	d	129.00	128.69	130.54
C-7	s	148.88	149.36	150.62
C-7a	s	173.68	178.16	174.16
C-9	d	75.58	74.42	74.50
C-10	d	41.68	40.84	30.84
OCH_3	s	52.05; 52.44		
C=O	s	170.50; 171.13	173.93; 174.41	
C≡N	s			115.31; 115.52

[a] From off resonance decoupled spectrum.

Upon prolonged standing in slightly acidic solution, **8a** underwent further transformations into **11** and **17**. This may be rationalized in terms of acid catalyzed ring opening of **8a** via **11** to **12**, which is in equilibrium with a chain of tautomers **14**, **17**, and **18**, dehydration of **12** would give **13**.

No tricyclic cyclohexadiene imine was obtained from **2b** and **6**. After allowing to react at 0 °C for 24 hours a 52% crop of **7b** was obtained along with 3% of **16** and 29% of **18**. It should be noted that benzenium-nitrenium ions **11** may be reached from both **7a,b** and **8a** and that all three compounds give rise to the same follow-up products via **12** and **14**.

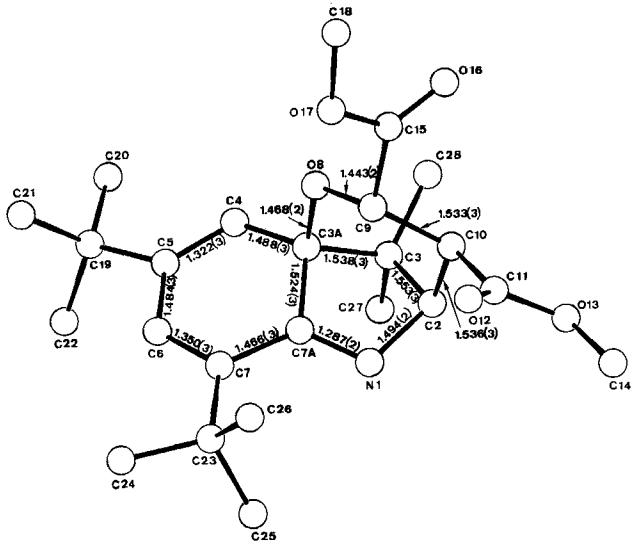


Figure 2. Molecular structure[8] of **8a** in the crystal (standard deviations of atomic distances given in parentheses)

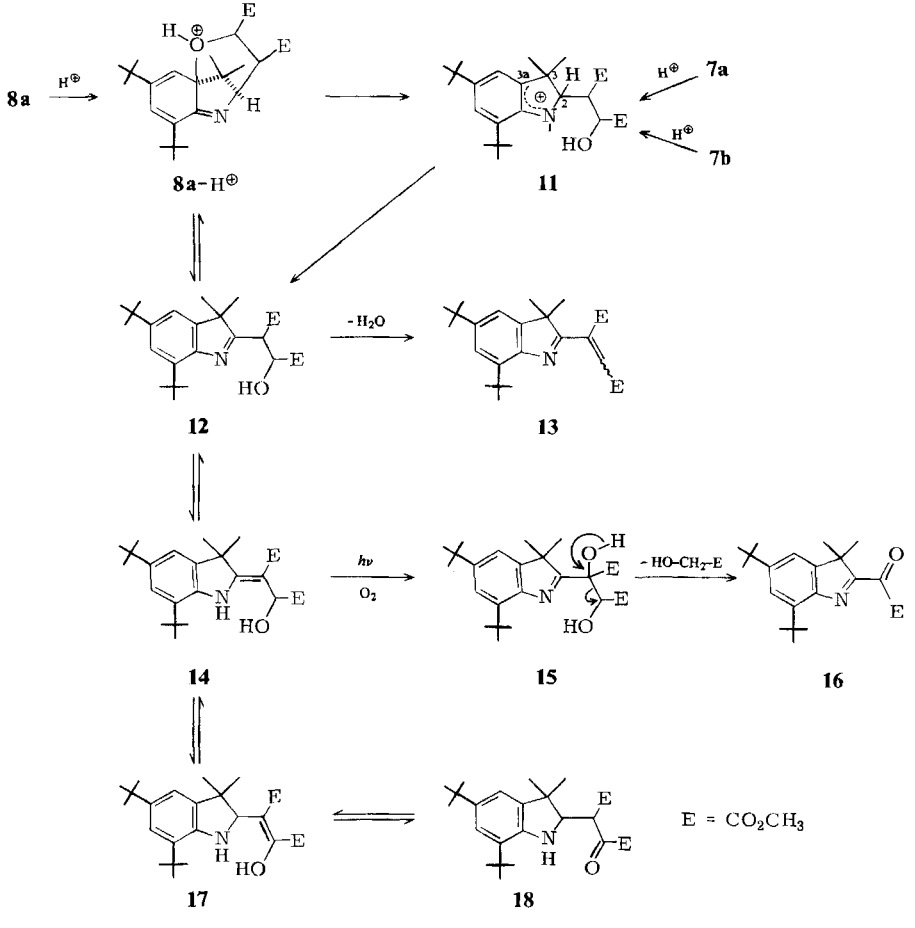
Table 4. Selected bond angles of compound **8a** (standard deviations given in parentheses)

N1 - C2 - C3	104.5(1)	C6 - C7 - C7a	114.9(2)
C2 - C3 - C3a	96.2(1)	C7 - C7a - C3a	120.2(2)
C3 - C3a - C7a	100.3(1)	C7a - C3a - O8	108.3(1)
C3a - C7a - N1	112.8(2)	C3a - O8 - C9	114.8(1)
C7a - N1 - C2	106.4(2)	O8 - C9 - C10	114.2(2)
C7a - C3a - C4	114.4(2)	C9 - C10 - C2	109.6(2)
C3a - C4 - C5	121.2(2)	C10 - C2 - C3	110.1(2)
C4 - C5 - C6	119.7(2)	C28 - C3 - C27	109.6(2)
C5 - C6 - C7	125.4(2)		
torsional angle	C15 - C9 - C10 - C11	80.42°	

7c could be isolated only when the components **6** and **2c** were allowed to react at −15°C, it decomposed upon attempted crystallization to give mainly **8c**. The latter was obtained directly in 91% yield upon reaction of **2c** with **6** at room temperature, along with 1.7% of an isomer of **8c**, to which structure **9** was assigned, and 2.3% of an *E,Z*-mixture of a yellow compound **10**, which appeared to arise from either **8c** or **9** or their respective precursors by acid catalyzed ring opening (analogous to that observed for **7a,b**, **8a**) and dehydrogenation of the ring opened species.

When **2c** was added to **6** in benzene, tetrahydrofuran or ethanol at reflux temperature, the yield of **9** tended to increase (benzene: 58% **8c**, 10% **9**, 2% **10**; tetrahydrofuran: 82% **8c**, 10% **9**, 2% **10**; ethanol: 52% **8c**, 15% **9**, 5% **10** (in addition, a 1:1:1 adduct of **2c**, **6** and ethanol had formed in low yield, the structure of which has

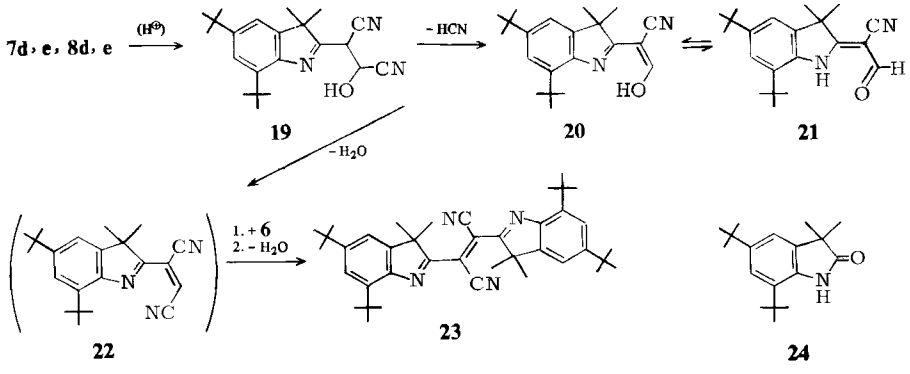
not yet been elucidated). Since **9** may be transformed quantitatively into **8c** in refluxing xylene within 24 hours, we are inclined to assign the less hindered structure to the obviously more stable isomer **8c** and the more crowded one to **9**.



No primary adducts **7d,e** could be isolated from the addition of either **2d** or **2e** to **6**, however, ^{1}H NMR signals attributable to **7d** could be detected within 10 minutes at 30°C after dissolving the components in $CDCl_3$. These signals soon gave way to those of **8d**. Preparative runs using one mmol of both components in methylene chloride at room temperature gave the following results: **6** + **2d**: 68% **8d**, 12.3% of the α-cyanoaldehyde **21**, 1.7% of **23** and 7% of lactam **24**; **6** + **2e**: only 23% of **8e**, 9.3% of **21** and 1.5% of **23**.

The structures of the by-products follow from their analytical and spectral data [**21**: IR (CCl_4): 3258, 3180 cm^{-1} (NH in bridge), 2870 and 2780 (CHO), 2220 (CN); **23**: *m/e* = 588 (M^+)], the formation of **21**, **23** can be rationalized in terms of (acid catalyzed?) ring opening of either **7d,e** or **8d,e** to **19**, which eliminates either hydrogen

cyanide to give **21** via **20** or water to give **22**. The latter in turn may undergo an analogous sequence of addition of **6** and loss of water to give finally **23**.



The structures of the main products **8c – e** and of **9** have been assigned in analogy to that of **8a** on the basis of their ^1H (table 2) and, if available, their ^{13}C NMR spectral data (table 3). The presence of only five sp^2-carbons in the six-membered ring together with the chemical shifts of the vinylic protons clearly show that the fused six-membered ring is no longer aromatic. The considerable upfield shift of the protons of one of the geminal methyl groups is noteworthy and highly probably due to the distortion around C-3a, which brings one of the C-3 methyl groups in a position above the dienoid π-system[9].

It is possible to follow the rearrangement **7c,d** → **8c,d** by ^1H NMR at ambient temperature in $CDCl_3$ solution. Under these conditions, **7c** has a half life of 15 min. So far, however, no temperature controlled measurements have been carried out.

Discussion

While the configuration at carbon atoms 9 and 10 has been rigorously established only for **8a**, configurational assignments can be made for **8c – e** only on the basis of the following assumptions.

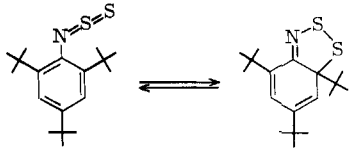
While the oxygen atom migrates – either stepwise or concertedly – from its position on nitrogen in **7** to its final position at C-3a in **8**, no configurational change should occur on the neighbouring carbon atoms (C-2 in **7** and C-9 in **8**, respectively). Thus the relative configuration of C-2, C-9, and C-10 in **8** should be identical with that of C-3a, C-2 and C-3 in **7**. There is no objection to assume that **7a** (of which an X-ray structural analysis could not be obtained) had the same relative configuration at C-3, C-3a as **3a**, which in turn is the one with the least infavourable interactions for a fumarate adduct. It is very likely that all main primary adducts of **6** – i.e. the isoxazolidines **7a – e** – have the same relative configuration at C-3, C-3a and that this relative configuration is uniformly maintained in compounds **8a, c – e**.

The rearrangement described is obviously highly promoted by steric overcrowding in the adducts **7**, especially between the 8-*tert*-butyl group and the fused isoxazolidine ring. Further promotion by acid has been demonstrated. Thus it is plausible to assume a stepwise process as outlined for **7a, b** involving a benzenium-nitrenium ion as **11** accessible through *O*-protonation and either N – O- or C – O-bond cleavage from **7a** or **8a**, respectively. Ions as **11** – being in fact

cyclized versions of *Gassman*'s "anilenium ions"[10a] – are susceptible to attack by nucleophiles at the ring carbons[10]. The only position, however, that can be reached by the intramolecular nucleophile (i.e. the hydroxyl group), is C-3a. Similar ions have been postulated in the acid mediated transformations of **1** and **6** accompanied by attack of external nucleophiles at C-5[4a]. Also, incorporation of chloroacetate at C-5 and opening of the isoxazolidine ring could be demonstrated upon treatment of the adduct derived from **1** and styrene with molten chloroacetic acid for two hours at 65 °C[2a,7].

Since ions like **11**, once formed from the crowded precursors **7a–e**, have the chance to react to "open" products as **10**, **12–18**, **19–24** instead of cyclizing to **8** which is (i) non aromatic and (ii) heavily distorted, one may be inclined to ask why they do so at all. It is possible that **11** and its analogues experience an easily accessible kinetically stabilized minimum at the geometry of **8**, which can be reached by migration of the protonated oxygen over a short distance, and unfavourable interactions between the 8-*tert*-butyl group and the isoxazolidine oxygen are reduced immediately. On the other hand, in the "outward" movement of the isoxazolidine oxygen may in its early stages *increase* the unfavourable interactions.

A close analogy to this case may certainly be found in the equilibrium **25** ⇄ **26**[11a].



25 **26**

26 certainly profits from reduction of steric repulsion between the C-2 and C-6 *tert*-butyl groups and the thiosulfinylamino group by changing C-6 from trigonal planar to tetrahedral. A similar effect seems to be operative in the reaction of Grignard reagents with 1,3,5-tri-*tert*-butylnitrobenzene, which – in part – leads to 2,4-cyclohexadienone oximes[11b].

Linearly conjugated cyclohexadiene imines are more abundant as intermediates[12–18] in various reactions than as stable entities[11a,19–28]. The ^{13}C and ^{1}H chemical shifts found for the cyclohexadienoid moiety of **8a,c–e** come very close to shift ranges for similar systems reported so far[11,21,22,25–28].

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Experimental Part

Melting points are uncorrected. – IR spectra: Beckman IR 20 A and Perkin-Elmer 397 and 283. Only characteristic bands are listed, very intense ones are given in italics, weak but relevant ones in parentheses. – UV spectra: Perkin-Elmer 554. – ^{1}H NMR spectra: Varian EM 360 (60 MHz) and EM 390 (90 MHz). – 75 MHz ^{13}C NMR spectra: Bruker WM 300. – EI-Mass spectra: MAT 311 and 311 A, temperature of inlet system given wherever available, only relevant peaks are listed. – Chromatography: 48 cm × 20 cm plates with 1 mm thick layers of silica gel Merck PF_{254}, air dry; number of plates required and solvent given. All yields refer to crystallized material.

Starting materials: 6-tert-Butyl-3,3-dimethyl-3H-indole 1-oxide (**1**)[4a] and *5,7-di-tert-butyl-3,3-dimethyl-3H-indole 1-oxide* (**6**)[4b] have been prepared according to published procedures.

Cycloadditions to 1

Dimethyl rel(2S,3S,3aR)-7-tert-butyl-2,3,3a,4-tetrahydro-4,4-dimethylisoxazolo[2,3-a]indole-2,3-dicarboxylate (**3a**): A solution of 108 mg (0.50 mmol) of **1** in 1 ml of benzene was added to a solution of 72 mg (0.50 mmol) of dimethyl fumarate (**2a**) in 1 ml of benzene and the mixture kept at 65 °C for 15 min. Crystallization of the residue from benzene/hexane gave 163 mg (90%), m.p. 115 °C. – IR (KBr): *1740* (C=O), *1270, 1242, 1219* cm^{-1}. – MS (70 eV): *m/e* = 361 (24%, M^+), 346(2), 331(2), 298(5), 286(20), 201(37), 200(72), 186(100), 171(28), 145(38), 113(52).

Table 5. Crystal data of **3a** and **8a**[8]

	3a	**8a**
formula	$C_{20}H_{27}NO_5$	$C_{24}H_{35}NO_5$
M_r	361.44	417.55
crystal size (mm)	0.54 × 0.50 × 0.18	0.25 × 0.11 × 0.18
a (Å)	9.829(3)	9.5173(8)
b (Å)	19.653(4)	10.1415(7)
c (Å)	10.456(2)	14.3345(5)
α (°)	90.	82.291(4)
β (°)	100.74(2)	73.103(3)
γ (°)	90.	66.925(6)
V (Å^3)	1984.3	1217.6
d_{calcd} (gcm^{-3})	1.21	1.14
Z	4	2
μ (cm^{-1})	0.81	6.03
space group (No.)	$P2_1/c$ (14)	$P\bar{1}$ (1)
radiation (Å)	(Mo)λ = 0.71069	(Cu)λ = 1.54178
diffractometer	Nonius CAD-4	Nonius CAD-4
unique refl.	4484	4849
observed refl.	2144	3249
ref. parameters	344	411
R	0.0503	0.0406
R_w	0.0454	0.0462

Dimethyl rel(2R,3S,3aR)-7-tert-butyl-2,3,3a,4-tetrahydro-4,4-dimethylisoxazolo[2,3-a]indole-2,3-dicarboxylate (**3b**): To a solution of 108 mg (0.50 mmol) of **1** in 1 ml of benzene were added 72 mg of dimethyl maleate (**2b**) and the mixture kept at 75 °C for 15 min. Crystallization of the residue from benzene/hexane gave 154 mg (85%), m.p. 135 °C. – IR (KBr): *1760* and *1740* (C=O), *1255* cm^{-1}. – MS (70 eV): *m/e* = 361 (14%, M^+), 346(1), 331(1), 298(5), 286(6), 226(16), 201(33), 200(48), 186(100), 171(28), 145(37), 113(17).

$C_{20}H_{27}NO_5$ (361.4) Calcd. C 66.46 H 7.53 N 3.88 **3a**: Found C 66.6 H 7.67 N 3.7
3b: Found C 66.38 H 7.60 N 3.81

rel(2R,3S,3aR)-7-tert-Butyl-2,3,3a,4-tetrahydro-4,4-dimethyl-N-phenylisoxazolo[2,3-a]indole-2,3-dicarboximide (**3c**): Solutions of 217 mg (1.0 mmol) of **1** and 173 mg (1 mmol) of *N*-phenylmaleic imide (**2c**) each in 1 ml of benzene were combined and kept at room temperature for 1 h. Crystallization from benzene gave 251 mg, m.p. 206–208 °C (dec.). Chromatography of the mother liquor (one plate, benzene/ethyl acetate 5:1) gave two zones, the first of which (R_F = 0.42) gave another 21 mg, m.p. 206–208 °C (dec.), total yield 271 mg (70%). – IR (KBr): (1790), *1720* (CO–N–CO), 1510, 1500, *1400, 1200* cm^{-1}, in addition, numerous low intense bands. – MS (70 eV): *m/e* = 390 (66%, M^+), 375(10), 373(8), 372(10), 217(33), 202(38), 201(18), 200(28), 186(63), 173(45), 132(95), 119(14), 78(38), 57(100).

rel(2S,3R,3aR)-7-tert-Butyl-2,3,3a,4-tetrahydro-4,4-dimethyl-N-phenylisoxazolo[2,3-a]indole-2,3-dicarboximide (**4**): The second zone (R_F = 0.14) gave 80 mg (21%), m.p. 120–121°C (from cyclohexane). – IR (KBr): (1788), *1725* (CO–N–CO), 1510, *1400, 1202* cm^{-1}. – MS (70 eV): *m/e* = 390 (47%, M^+), 375(7), 217(71), 202(45), 200(25), 173(90), 161(60), 132(81), 57(100).

$C_{24}H_{26}N_2O_3$ (390.5) Calcd. C 73.82 H 6.71 N 7.18 **3c**: Found C 73.9 H 6.72 N 7.0
4: Found C 73.8 H 6.80 N 7.06

6-tert-Butyl-3,3a-dihydro-3,3-dimethyl-N-phenyl-2,3a-(epoxyethano)-2H-indole-9,10-dicarboximide (**5**): In another run, 1.00 g (4.60 mmol) of **1** and 796 mg (4.60 mmol) of **2c** were dissolved in 3 ml of benzene and left standing at ambient temperature overnight. The precipitate (1.128 g of **3c**, m.p. 206–208°C with dec.) was filtered off. The mother liquors were concentrated and the residue chromatographed on two plates (toluene/ethyl acetate 5:1) to give another crop of 180 mg of **3c** (total yield thus 1.308 g (73%)), 347 mg (19.3%) of **4** and 32 mg (1.8%, migrating between **3c** and **4**) of a crystalline compound, m.p. range 230–235°C (from benzene, with dec.). – IR (KBr): (1782), 1712 (CO–N–CO), 1500, *1395, 1200,* 1108 cm^{-1}. In addition, numerous low and medium intense bands are present. – 60 MHz ^1H NMR ($CDCl_3$, TMS): δ = 0.88 (s, 3H, CH_3), 1.18 (s, 9H, $C(CH_3)_3$), 1.35 (s, 3H, CH_3), 3.52 (dd, $^3J_{2,10}$ = 3.6 Hz, $^3J_{9,10}$ = 8.4 Hz, 10-H), 4.45 (d, J = 3.6 Hz, 2-H), 4.70 (d, J = 8.4 Hz, 9-H), AB (δ_A = 6.55, δ_B = 6.06, J_{AB} = 10.0 Hz, A-signals additionally split by 1.4 Hz, B-signals by approximately 1 Hz), 6.27 (mc, 1H), 7.40 (mc, 5H, *N*-phenyl). – MS (70 eV, 135°C): *m/e* = 390 (60%, M^+), 375(26), 362(18), 361(12), 359(7), 347(45), 334(18), 333(12), 228(9), 217(22), 216(14), 202(100), 187(60), 186(54), 146(46), 57(40).

$C_{24}H_{26}N_2O_3$ (390.5) Calcd. C 73.82 H 6.71 N 7.18 Found C 73.58 H 6.71 N 7.21

rel(2S,3S,3aR)-7-tert-Butyl-2,3,3a,4-tetrahydro-4,4-dimethylisoxazolo[2,3-a]indole-2,3-dicarbonitrile (**3d**): To a solution of 108 mg (0.5 mmol) of **1** in 1 ml of dry benzene 39 mg (0.5 mmol) of fumarodinitrile (**2d**) were added and the mixture left standing at room temperature for 2 h. Chromatography (2 plates, benzene/ethyl acetate 10:1) gave two zones, the second one of which (R_F = 0.39) contained too little material and was therefore discarded. The first zone (R_F = 0.50) gave 116 mg (79%), m.p. 125°C (with dec., from benzene/hexane). – IR (KBr): 2270 (CN), 1625, 1495, 1420, 1375, 845 cm^{-1}. – MS (19 eV): *m/e* = 295 (18%, M^+), 280(2), 268(6), 253(6), 240(10), 225(11), 217(23), 201(56), 186(100), 161(35), 145(36), 78(14), 57(15).

$C_{18}H_{21}N_3O$ (295.4) Calcd. C 73.19 H 14.23 N 7.17 Found C 72.94 H 14.34 N 7.16

Conversion of **4** *into* **3c**: 10 mg samples of **4** and **3c** were each dissolved in 10 ml of *m*-xylene and the solutions heated to reflux for 45 min, concentrated and chromatographed (one half plate each, benzene/ethyl acetate 10:1). While the sample of **3c** had remained entirely unchanged, 50% of **4** had been converted into **3c** (m.p., IR-comparison).

Cycloadditions to 6

Dimethyl rel(2S,3S,3aR)-6,8-di-tert-butyl-2,3,3a,4-tetrahydro-4,4-dimethylisoxazolo[2,3-a]indole-2,3-dicarboxylate (**7a**): To a solution of 273 mg (1 mmol) of **6** in 1 ml of methylene chloride at 0°C is added a chilled solution of 154 mg (1.07 mmol) of freshly sublimed **2a** in 2 ml of methylene chloride. The mixture was kept at 0°C for 24 h, during which time it assumed a brownish colour. The solution was concentrated at 0°C, the brown residue was treated with 3 ml of cold pentane to yield 310 mg (74%) of colourless crystals, m.p. 106°C. – IR (KBr): 2970, *1745* and *1725* (CO), 1270, 1250, 1240, 1010 cm^{-1}. – MS (70 eV, 92°C): *m/e* = 417 (M^+, 17%), 343(26), 329(78), 314(43), 297(26), 288(100), 258(96), 241(96), 200(39), 186(74), 57(52). – UV (cyclohexane): λ_{max} (lg ε) = 248 (broad, 3.62), 221 (4.12) nm.

$C_{24}H_{35}NO_5$ (417.5) Calcd. C 69.04 H 8.45 N 3.35 Found C 68.74 H 8.48 N 3.32

Dimethyl rel(2R,3aS,9S,10S)-5,7-di-tert-butyl-3,3a-dihydro-3,3-dimethyl-3a,2-(epoxyethano)-2H-indole-9,10-dicarboxylate (**8a**): In another run using the same quantities of **2a**, **6** and solvent as given before, the mixture was allowed to warm to room temperature before concentrating. The yellow-brownish mixture was separated using three plates with toluene/ethyl acetate (5:1) into eight zones. From the main one at R_F = 0.50 175 mg (42%) of crystals, m.p. 190–195°C, were isolated, which, after crystallization from ethyl acetate, gave 155 mg (37%) of colourless crystals, m.p. 200°C, which may be sublimed in high vacuum at 130–140°C without decomposition. – IR (KBr): *2950, 1735* (CO), 1580, 1440, 1298, *1235*, 1178, 1035, 1015 cm^{-1}. – MS (70 eV, 132°C): *m/e* = 417 (M^+, 65%), 402(60), 358(56), 329(31), 314(21), 282(21), 258(100), 256(82), 242(67), 200(91), 186(62), 57(87). – UV (cyclohexane): λ_{max} (lg ε) = 309 (3.55), 240 (sh, 3.44), 216 (sh, 3.73), λ_{min} = 266 nm (3.13).

$C_{24}H_{35}NO_5$ (417.5) Calcd. C 69.04 H 8.45 N 3.35 Found C 69.02 H 8.40 N 3.36

The sixth zone (R_F = 0.35) gave 10 mg (3.6%) of *5,7-Di-tert-butyl-3,3-dimethyl-2-indolinone* (**24**), m.p. 241°C (lit.[29] 240–241°C), the seventh (R_F = 0.30) 10 mg (2.4%) of **18** (by IR-comparison, see below).

Dimethyl rel(2R,3S,3aR)-6,8-di-tert-butyl-2,3,3a,4-tetrahydro-4,4-dimethylisoxazolo[2,3-a]-indole-2,3-dicarboxylate (**7b**): To a chilled (0°C) solution of 273 mg (1 mmol) of **6** in 2 ml of methylene chloride a solution of 154 mg (1.07 mmol) of **2b** in 2 ml of the same solvent is added and the mixture kept standing at 0°C for 24 h. The solution is concentrated in vacuo at 0°C, the residue is treated at –15°C with pentane to give 220 mg (52%) of colourless needles, m.p. 88°C. – IR (KBr): *2960,* 2900, 2860, *1730* and 1720 (CO), 1480, 1458, 1440, 1373, 1365, 1303, 1210, 1175 cm^{-1}. – MS (70 eV, 108°C): *m/e* = 417 (4%, M^+), 358(2), 329(24), 314(16), 298(10), 297(12), 282(37), 257(53), 256(12), 255(8), 241(100), 215(24), 200(33), 185(86), 171(16), 158(28), 101(37), 59(27), 57(28). – UV (cyclohexane): λ_{max} (lg ε) = 280 (sh, 3.09), 246 (3.75), 220 (4.0) nm.

$C_{24}H_{35}NO_5$ (417.6) Calcd. C 69.04 H 8.45 N 3.35 Found C 68.99 H 8.69 N 3.33

The mother liquor was separated on three plates with toluene/ethyl acetate into 7 zones, the first, third and seventh of which were discarded due to very low intensity. The fifth zone (R_F = 0.3) gave 7.2 mg (2.6%) of **24** (IR-comparison).

Methyl (5,7-di-tert-butyl-3,3-dimethyl-3H-indol-2-yl)glyoxylate (**16**): From the second zone (R_F = 0.7) 10 mg (3%) of light green crystals, m.p. 160–161°C (pentane), are isolated. – IR (KBr): 2960, *1745* (CO), 1680 (CO), 1362, 1258, 1122, 986 cm^{-1}. – 60 MHz ^1H NMR ($CDCl_3$, TMS): δ = 1.37 (s, 9H, *t*Bu), 1.50 (s, 6H, CMe_2), 1.53 (s, 9H, *t*Bu), 4.00 (s, 3H, OCH_3), 7.27 and 7.43 (two d, *J* = 2 Hz, 2H, Aryl). – MS (70 eV, 98°C): *m/e* = 343 (100%, M^+), 328(57), 284(70), 268(45), 256, 255, 254 (32 each), 241(27), 240(50), 226(43), 212(32), 200(45), 57(43).

$C_{21}H_{29}NO_3$ (343.4) Calcd. C 73.44 H 8.51 N 4.08 Found C 73.10 H 8.68 N 4.15

Dimethyl (5,7-di-tert-butyl-3,3-dimethyl-2-indolinyl)oxalacetate (**18**): The material from the sixth zone (non fluorescence quenching, main zone, R_F = 0.20) gives 120 mg (29%), m.p. 146°C (from pentane). – IR (KBr): 3508 (sharp) and 3290 (broad, NH), *1730* and *1662* (CO), *1578*, 1480, 1435, 1273, 1255, 1230, 1200, 1180, 1150, 1072 cm^{-1}. – (CCl_4, *d* = 3 cm): 3468 (NH), 3284 cm^{-1} (NH?). – 60 MHz ^1H NMR ($CDCl_3$): δ = 1.33 (s, 9H, CMe_3), 1.43 (s, 9H, CMe_3); 1.58 (s, 3H) and 1.65 (s, 3H, gem. CMe_2); 3.43 (d, *J* = 6.4 Hz, $CH-CO_2CH_3$, signal fades upon D_2O-treatment of sample solution), 5.23 (d, *J* = 6.4 Hz, 1H, 2-H, collapses to singlet upon D_2O treatment), AX (δ_A = 7.10, δ_X = 7.23, *J* = 2 Hz, 2H, Aryl-H), 11.27 (broad, 1H, NH). – MS (70 eV, 131°C): *m/e* = 417 (11%, M^+), 399(39), 384(21), 368(21), 367(43), 358(32), 352(21),

340(36), 339(36), 329(64), 326(36), 314(39), 297(29), 282(100), 256(25), 255(32), 254(19), 242(19), 57(21).

$C_{24}H_{35}NO_5$ (417.5) Calcd. C 69.04 H 8.45 N 3.35 Found C 68.50 H 8.43 N 3.42

Dimethyl E-(or Z)-(5,7-di-tert-butyl-3,3-dimethyl-3H-indol-2-yl)ethenedicarboxylate (**13**): A 80 mg sample (0.19 mmol) of **18** in 10 ml of methylene chloride was agitated with 5 ml of conc. H_2SO_4 at −15°C for 15 min, during which time the acid layer assumed a red colour. After quenching with ice/water, the methylene chloride layer was separated, dried, concentrated and the residue separated (1 plate, toluene/ethyl acetate) into two zones. The second zone (R_F = 0.20) gave 20 mg of **18**, the first zone (R_F = 0.40) 47 mg (62%) of m.p. 137°C (pentane). – IR (KBr): *1752* and *1723* (CO), 1620 (C=C) cm^{-1}. – 60 MHz ^1H NMR ($CDCl_3$): δ = 1.40 (s, 9H, CMe_3), 1.50 (s, 6H, CMe_2), 1.55 (s, 9H, CMe_3), 3.85 (s, 3H, OMe), 4.00 (s, 3H, OMe), 6.50 (s, 1H, vinyl-H), AX (δ_A = 7.23, δ_X = 7.40, J = 2.0 Hz, Aryl-H). – MS (70 eV, 82°C): *m/e* = 399 (100%, M^+), 384(81), 376(73), 352(18), 340(45), 339(36), 329(18), 57(81).

$C_{24}H_{33}NO_4$ (399.3) Calcd. C 72.15 H 8.32 N 3.50 Found C 72.10 H 8.33 N 3.50

Photooxidation of **18**: A 40 mg sample (0.096 mmol) in 10 ml of methylene chloride was irradiated under reflux and an oxygen atmosphere from a distance of 30 cm with a 300 W Osram vitalux (sunlight simulation) lamp for two days. A blank was set aside for the same time. Separation of the illuminated sample (1 plate, toluene/ethyl acetate 5:1) gave three zones, the slowest one of which contained small amounts of residual **18** (IR-comparison), the second (R_F = 0.40) small quantities of **13**. From the first zone (R_F = 0.65) 25 mg (76%) of **16**, m.p. 160°C, identical by its IR and ^1H NMR with the material reported above.

8a *from* **7a**: As was demonstrated by ^1H NMR, a sample solution of **7a** is transformed into a solution of **8a** within two days at ambient temperature. If one crystal of *p*-toluenesulfonic acid is added to the sample solution, the **7a** → **8a** conversion is completed within one hour.

Decomposition of **8a**: As followed by ^1H NMR, a sample solution ($CDCl_3$) prepared from **8a** containing catalytic amounts of *p*-toluenesulfonic acid contains mainly **18** after two days, accompanied by minor amounts of **13**. Prolonged standing at ambient temperature increases the fraction of the latter compound.

rel(2R,3S,3aR)-6,8-Di-tert-butyl-2,3,3a,4-tetrahydro-4,4-dimethyl-N-phenylisoxazolo[2,3-a]-indole-2,3-dicarboximide (**7c**): Solutions of 273 mg of **6** and 173 mg of **2c** (1.0 mmol each) in 2 ml of methylene chloride are mixed at −15°C and kept for 14 h at this temperature. Concentration in the cold and addition of cold pentane gave 210 mg (47%) of crystals, m.p. 115°C, which underwent conversion into **8c** (see below) upon attempted recrystallization. – IR (KBr): 2958, 2900, 2868, (1790), *1720*, 1600, 1500, 1478, 1458, 1382, 1364, 1195, 1070, 732, 692 cm^{-1}.

rel(2R,3aS,9R,10S)-5,7-Di-tert-butyl-3,3a-dihydro-3,3-dimethyl-N-phenyl-3a,2-(epoxyethano)-2H-indole-9,10-dicarboximide (**8c**): 273 mg of **6** and 173 mg of **2c** (1.0 mmol each) were dissolved in 2 ml of methylene chloride and the mixture left standing at room temperature for 2 h, after which time the solvent was removed i. vac. and the residue treated with 5 ml of pentane to give 360 mg (81%) of colourless crystals, m.p. 220–222°C (from cyclohexane). – IR (KBr): 2955, 2900, 2865, (1790), *1715* (CO), 1568, 1497, 1458, 1390, 1370, 1200, 1180, 1100, 755, 692 cm^{-1}. – UV (cyclohexane): λ_{max} (lg ε) = 298 (3.44), 225 (4.23), broad plateau from 306 (3.42) to 330 (3.34) nm, λ_{min} = 272 nm (3.25). – MS (70 eV): *m/e* = 446 (13%, M^+), 431(12), 404(3), 403(2), 390(2), 389(3), 299(3), 298(4), 284(8), 273(5), 258(20), 256(18), 242(12), 200(27), 187(15), 119(30), 91(21), 77(22), 57(100).

$C_{28}H_{34}N_2O_3$ (446.6) Calcd. C 75.30 H 7.67 N 6.27 Found C 75.2 H 7.70 N 6.1

The mother liquors (80 mg residue) were separated on one plate with toluene/ethyl acetate (10:1) into 6 zones, the three fastest moving of which were discarded due to their low material content. The slowest zone gave another 47 mg (10%) of colourless crystals of **8c**, m.p. 200–222 °C (from petroleum ether b.p. 60–70 °C).

rel(2R,3aS,9S,10R)-5,7-Di-tert-butyl-3,3a-dihydro-3,3-dimethyl-N-phenyl-3a,2-(epoxyethano)-2H-indole-9,10-dicarboximide (**9**): The fifth zone (R_F = 0.35) gave 7.6 mg (1.7%) of colourless crystals, m.p. 208–210 °C (benzene/pentane). – IR (KBr): 2960, 2930, 2900, 2870; (1782), *1720* and *1710* (CO); 1572, 1500, *1388, 1192,* 1018, 732, 692 cm^{-1}. – MS (70 eV): *m/e* = 446 (41%, M^+), 431(45), 404(17), 390(15), 389(16), 299(9), 273(12), 258(47), 256(12), 242(32), 200(41), 190(25), 157(18), 146(14), 119(12), 77(83), 57(100).

$C_{28}H_{34}N_2O_3$ (446.6) Calcd. C 75.30 H 7.67 N 6.27 Found C 75.30 H 7.69 N 6.10

(E,Z)-4-(5,7-Di-tert-butyl-3,3-dimethyl-2-indolinylidene)-1-phenyl-2,3,5-pyrrolidinetrione (**10**): The fourth zone (R_F = 0.42) gave 10 mg (2.3%) of yellow crystals, melting range 230–235 °C (from pentane). – IR (KBr): 3270 (broad, NH), 1775, *1720, 1655, 1570,* 1502, *1382* cm^{-1}, numerous additional medium and low intense bands. – (CCl_4): 3280 (broad), 1780, 1720, *1670, 1565, 1380* cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 1.33 (s, 18H), 1.44 (s, 9H), 1.52 (s, 9H), 1.80 (mc, 12H, 3-$(CH_3)_2$, 7.34 (mc, 4H) and 7.50 (mc, 10H, aryl-H), 11.85 and 12.90 (broad, 1H each, NH). – (C_6D_6): δ = 1.24, 1.26, 1.30 and 1.38 (four s, 9H each, *tert*-butyl), 1.61 and 1.71 (two s, 6H each, 3-$(CH_3)_2$), aryl signals perturbed by solvent signals, 12.20 and 13.12 (two broad signals, 1H each, NH). – MS (70 eV): *m/e* = 444 (100%, M^+), 443(25), 429(83), 415(8), 402(9), 373(23), 372(10), 357(7), 297(25), 296(25), 295(14), 282(48), 57(35).

$C_{28}H_{32}N_2O_3$ (444.6) Calcd. C 75.65 H 7.26 N 6.30 Found C 75.5 H 7.21 N 6.0

Reaction of **6** *with* **2c** *in various solvents at reflux temperature:* Solutions of 1 mmol each of both components in 4 ml of the solvents given below were refluxed for 2 h and allowed to cool. The crystalline precipitate of the main product **8c** was collected and the mother liquors separated using 5 plates each with benzene/ethyl acetate (10:1) into five zones, the fifth and third of which were discarded. The fourth zone (R_F = 0.26) always gave additional **8c**, while **9** was isolated from the second (R_F = 0.50) and **10** from the first zone (R_F = 0.58). The following amounts of material have been obtained and are given in the order of solvent used (benzene, tetrahydrofuran, ethanol): **8c**: 259 mg (58%), 366 mg (82%), 232 mg (52%), m.p. 220–222 °C; **9**: 45 mg (10%), 44 mg (10%), 67 mg (15%), m.p. 208–210 °C; **10**: 9 mg (2%), 9 mg (2%), 22 mg (5%), m.p. 231–235 °C.

Conversion of **9** *into* **8c**: Solutions of 10 mg samples each of **8c** and **9** in 10 ml of *m*-xylene were kept at reflux temperature for 24 h. While **8c** was recovered unchanged from the solution, **9** had been quantitatively transformed into **8c**, m.p. 220–222 °C, its IR being identical with that of an authentic sample.

Cycloaddition of fumarodinitrile (**2d**) *to* **6**: A solution of 273 mg (1.0 mmol) of **6** and 78 mg (1.0 mmol) of **2d** in 2 ml of methylene chloride was left standing 3 h at room temperature. The solution, which readily had assumed an orange-red colour, was concentrated and the residue separated by chromatography using three plates and cyclohexane/ethyl acetate (5:1) into four zones, the slowest one of which contained 20 mg (7%) of **24**, m.p. 242 °C (lit.[29] 240–241 °C), the IR being identical with that of an authentic sample.

2,3-Bis(5,7-di-tert-butyl-3,3-dimethyl-3H-indol-2-yl)fumarodinitrile (**23**): From the first intensely red zone (R_F = 0.6) 5 mg (1.7%) of red crystals, m.p. 300–301 °C (from pentane) were obtained. – IR (KBr): *2960,* 2900, 2870, 2210 (CN), 1600, *1495,* 1480, 1462, 1400, *1362,* 1242, 1230, 1125, 1055, 960, 882, 790 cm^{-1}. – UV (methylene chloride): λ_{max} (lg ε) = 470 (4.29),

260 (4.0) nm. – ^{1}H NMR ($CDCl_3$): δ = 1.40 (s, 18H) and 1.62 (s, 18H, *tert*-butyl); 1.64 (s, 12H, $C(CH_3)_2$); 7.30 (mc, 2H) and 7.45 (mc, 2H, aryl-H). – MS (70 eV, 117°C): *m/e* = 588 (98%, M^+), 573(99), 568(44), 556(60), 548(100), 57(28).

$C_{40}H_{52}N_4$ (588.9) Calcd. C 81.85 H 8.90 Found C 80.73 H 8.77

2-(5,7-Di-tert-butyl-3,3-dimethyl-2-indolinylidene)-2-formylacetonitrile (**21**): From the second zone (R_F = 0.35) 40 mg (12%), m.p. 198–200°C (from pentane) were isolated. – IR (KBr): Several weak absorptions between 3400 and 2400 cm^{-1} (NH?), 2970, 2870 and 2780 (CHO), 2220 (CN), *1640*, 1612, *1550*, 1210, 1175, 767 cm^{-1}. – (CCl_4, *d* = 3 cm): 3258, 3180 cm^{-1} (NH). – ^{1}H NMR ($CDCl_3$): δ = 1.37 (s, 9H, *tert*-butyl), 1.50 (s, 9H, *tert*-butyl), 1.70 (s, 6H, CMe_2); 7.23 (mc, 2H) and 7.33 (mc, 2H, aryl-H); 9.46 (s, 1H, CHO), 13.00 (broad, 1H, NH). – MS (70 eV, 44°C): *m/e* = 324 (57%, M^+), 323(10), 310(50), 309(100), 295(14), 294(15), 281(10), 279(15), 253(10), 238(5), 209(5).

$C_{21}H_{28}N_2O$ (324.4) Calcd. C 77.73 H 8.70 N 8.63 Found C 77.18 H 8.77 N 8.87

rel(2R,3aS,9S,10S)-5,7-Di-tert-butyl-3,3a-dihydro-3,3-dimethyl-3a,2-(epoxyethano)-2H-indole-9,10-dicarbonitrile (**8d**): The third (and main) zone (R_F = 0.24) gave 220 mg (68%) colourless crystals, m.p. 181–182°C (with dec., from pentane). – IR (KBr): *2960*, 2870, 2250 (CN), (1645), 1568, 1475, 1465, 1390, 1365, 1260 and numerous medium intense bands between 1100 and 600 cm^{-1}. – UV (cyclohexane): λ_{max} (lg ε) = 318 (3.54), 234 (sh, 3.50), 215 (sh, 3.73) nm, λ_{min} = 270 nm (3.04). – MS (70 eV, 121°C): *m/e* = 351 (100%, M^+), 336(70), 296(61), 281(78), 258(78), 256(43), 242(43), 218(78), 200(87), 186(30), 84(70), 57(87), 56(70).

$C_{22}H_{29}N_3O$ (351.5) Calcd. C 75.18 H 8.32 N 11.95 Found C 75.05 H 8.26 N 11.96

^{1}H NMR spectroscopic detection of rel(2S,3S,3aR)-6,8-di-tert-butyl-2,3,3a,4-tetrahydro-4,4-dimethylisoxazolo[2,3-a]indole-2,3-dicarbonitrile (**7d**): A sample solution containing 25 mg of **2d** and 87.5 mg of **6** (0.32 mmol each) in 0.4 ml of $CDCl_3$ was kept at ambient temperature. After 10 min, the signals reported in table 1 appeared and soon gave way to the signals of **8d** (table 2), which clearly was the main component of the mixture after 1.5 h.

Cycloaddition of maleodinitrile (**2e**) *to* **6**: 273 mg (1.0 mmol) of **6** and 100 mg of crude **2e** containing 14% of fumarodinitrile (**2d**) from ^{1}H NMR integration, m.p. 33–35°C (lit.[30] 31–32°C)) were dissolved in 2 ml of methylene chloride and the mixture left standing 3 h at room temperature, during which time it assumed an orange-red colour. The concentrate was separated on three plates using cyclohexane/ethyl acetate (5:1) into 8 zones. From the first (red) zone (R_F = 0.65), 2 mg of **23** were isolated, m.p. 301°C, the IR being identical with that of the sample reported above. The fourth zone (R_F = 0.40) gave 30 mg (9%) of **21**, m.p. 198–200°C, the IR being identical with that of the sample reported above. All other zones, except the slowest moving one, were discarded due to low material content.

rel(2R,3aS,9R,10S)-5,7-Di-tert-butyl-3,3a-dihydro-3,3-dimethyl-3a,2-(epoxyethano)-2H-indole-9,10-dicarbonitrile (**8e**): From the last zone (R_F = 0.15) 80 mg (23%) of colourless crystals, m.p. 184–185°C (from pentane) were isolated. – IR (KBr): 2960, 2900, 2870, 2250 (CN), *1565*, 1480, 1465, 1392, 1370, 1260, 1062, 935, 872 cm^{-1}. – UV (cyclohexane): λ_{max} (lg ε) = 321 (3.48), 240 (sh), 215 (sh, 3.72) nm. – MS (70 eV, 70°C): *m/e* = 351 (17%, M^+), 336(34), 324(17), 309(55), 296(10), 295(7), 294(7), 281(41), 258(26), 257(31), 242(59), 200(100), 186(62), 158(27), 145(31), 57(65).

$C_{22}H_{29}N_3O$ (351.5) Calcd. C 75.18 H 8.32 N 11.95 Found C 75.32 H 8.62 N 11.20

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