Generation and Characterization of Transient 3*H*-Indolium-methanides[1)]

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Transient 3*H*-indolium-methanides **3a–d** have been generated from the corresponding 2-substituted 3*H*-indoles **1a–d** by the *N*-(trimethylsilyl)methylation/desilylation method. **3a,b** were trapped by dimethyl maleate and dimethyl fumarate stereospecifically. All ylides add dimethyl ethynedicarboxylate to form 9,9a-dihydro-3*H*-pyrrolo[1,2-*a*]indoles **11a–d**, out of which **11c,d** (R = 9a-alkoxy) readily eliminate the corresponding alkanols to form **12**. In the absence of dipolarophiles, **1a** is predominantly transformed into Fischer base **14**, whereas **3b** gives rise to an unsymmetrical dimer **16**.

Darstellung und Charakterisierung transienter 3*H*-Indolium-methanide[1)]

Die transienten 3*H*-Indolium-methanide **3a,d** wurden aus den entsprechenden 2-substituierten 3*H*-Indolen **1a–d** durch *N*-(Trimethylsilyl)methylierung und Desilylierung erzeugt. **3a,b** werden stereospezifisch mit Dimethyl-maleat bzw. -fumarat abgefangen. Alle genannten Ylide addieren Dimethyl-ethindicarboxylat, wobei die 9,9a-Dihydro-3*H*-pyrrolo[1,2-*a*]indole **11a–d** gebildet werden, von denen **11c,d** (R = 9a-alkoxy) sofort die entsprechenden Alkanole unter Bildung von **12** abspalten. In Abwesenheit von Dipolarophilen wird **1a** hauptsächlich in die Fischer-Base **14** übergeführt, während **3b** ein unsymmetrisches Dimer **16** bildet.

During the course of investigations of the chemical behaviour of 3*H*-indole 1-oxides[2)] we became interested in an access to the corresponding 3*H*-indolium-1-methanides, which had been unknown until recently[3)]. 1,3-Dipolar cycloadditions of both alkenes and alkynes to 3*H*-indolium-ylides provide access to pyrrolo[1,2-*a*]indoles[3)], the basic structural unit of mitomycins[4)]. Although this particular aspect has already been treated by other authors[3)], we describe in this paper our experiences in the preparation and some cycloadditions of the elusive 2-substituted methanides **3a–d**. For preparation of the latter, the now well-established silylmethylation–desilylation method[5)] has been used, which already has been applied successfully to a variety of both acyclic and cyclic imines[3a,5)].

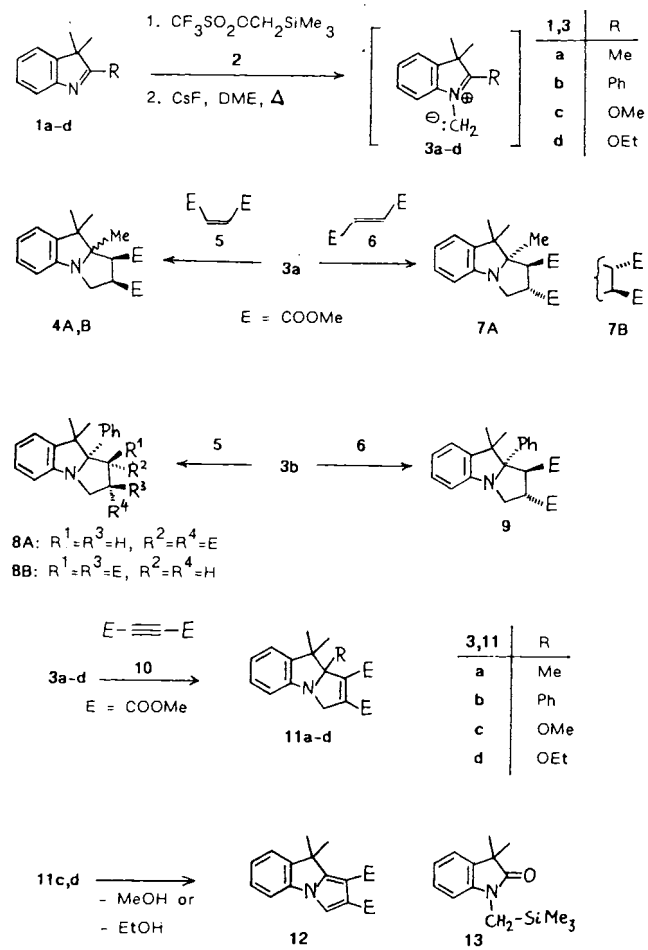
Results and Discussion

Trapping of 3a–d with Unsaturated Diesters

N-Alkylation of 3*H*-indoles **1a–d** with (trimethylsilyl)-methyl trifluoromethane sulfonate (**2**) gave the corresponding *N*-[(trimethylsilyl)methyl]-3*H*-indolium salts. Strong support that desilylation[5)] of the latter by caesium fluoride liberated the 3*H*-indolium-1-methanides **3a–d** comes from the various trapping products (**4**, **7–12**), and it is generally assumed henceforth in this paper that the ylides **3a–d** are indeed formed in the desilylation step.

From **3a** with dimethyl maleate (**5**) an oily 9:1 mixture (as delineated from the ^{1}H-NMR integral) of two 1:1 adducts (**4A,B**) was obtained. From comparison of the 300-MHz ^{1}H-NMR spectrum of the **4A, 4B** mixture with the spectra of the adducts **7A** and **7B** obtained from **3a** and dimethyl fumarate (**6**, vide infra), it followed that neither **4A** nor **4B** were identical to any of the fumarate adducts. A satisfactory assignment of the structures of **4A** and **4B** could not be made due to an unfortunate overlap of signals in the ^{1}H-NMR spectrum.

Scheme 1



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On the other hand, addition of dimethyl fumarate (**6**) to **3a** gave two crystalline adducts **7A** (32%) and **7B** (43%) which could be separated by preparative layer chromatography. The 300-MHz ^{1}H-NMR spectrum of **7A** as well as that of **7B** did not show any signals as found in the ^{1}H-NMR spectrum of the oily **4A, 4B** mixture. Again, an unambiguous structural assignment of **7A** and **7B** based on their ^{1}H-NMR data did not seem to be justified.

Similarly, from **3b** with dimethyl maleate (**5**) a mixture of two separable adducts **8A** (crystalline, 24% yield) and **8B** (oily, 29%, yields refer to chromatographically separated material) resulted. The recovered dipolarophile, however, consisted of a 2:1 mixture of dimethyl maleate (**5**) and dimethyl fumarate (**6**).

Trapping of **3b** with **6**, on the other hand, gave only one product (**9**, 72%), which was different from either **8A** or **8B**.

From their 300-MHz ^{1}H-NMR spectra, the structures of **8A, 8B** and **9** are derived on the basis of the following observations (see Table 1) and considerations: For **8B** and **9** the multiplets assigned to the 9a-phenyl hydrogens are partially broadened due to hindered rotation around the C9a-phenyl bond[6]. **8A,** however, shows a series of sharp multiplets for the 9a-phenyl hydrogens and at the same time a distinct upfield shift for one of the $COOCH_3$ singlets. This suggests that the 9a-phenyl group is tightly embedded between one of the 9-CH_3 groups and the 1-methoxycarbonyl group, which brings the latter into the shielding region of the phenyl ring and at the same time effectively suppresses any torsional freedom of this group. In **8B**, due to torsional mobility of the 9a-phenyl group, 1-H may experience the deshielding influence of the latter, while neither methoxy carbonyl group is influenced by the shielding effect. In **9**, shielding and deshielding effects of 9a-phenyl on 1-H may well cancel out.

Table 1. Characteristic ^{1}H-NMR features of compounds **8A, 8B, 9**

	Appearance of 9a-phenyl signals	$COOCH_3$ (δ, ppm)		3-H (δ, ppm)
8A	several sharp multiplets	3.04	3.54	3.55
8B	broadened	3.27	3.51	3.86
9	broadened	3.55	3.66	3.50

In all cases mentioned so far, the mother liquors or distillation residues did not show the presence of other stereoisomers of the products isolated.

Although it may seem unsatisfactory at first glance that define structural assignments could not be made for compounds **4A, 4B, 7A,** and **7B**, it may still be concluded with caution that **5** and **6** are added stereospecifically to **3a** and **3b**.

Under otherwise the same conditions, **3a–d** were trapped by dimethyl ethynedicarboxylate (**10**) to form 9,9a-dihydro-3*H*-pyrrolo[1,2-*a*]indoles **11a–d**.

Whereas **11a** and **11b** may be collected in yields of 82 and 66%, respectively, compounds **11c,d** could not be isolated, probably due to spontaneous elimination of methanol or ethanol with formation of the 9*H*-pyrrolo[1,2-*a*]indole **12**, which is isolated in only 21–25% yield. These low yields are probably due to dealkylation on oxygen in the *N*-trimethylsilylation process and formation of the indolinone **13**, which has been obtained in 61% yield from **1d** when treated with **2** in the absence of dipolarophiles. This *O*-dealkylation coupled to *N*-alkylation is well-documented for imidates[7]. The structures of **11a,b, 12,** and **13** are in complete accord with their spectroscopic and analytical data.

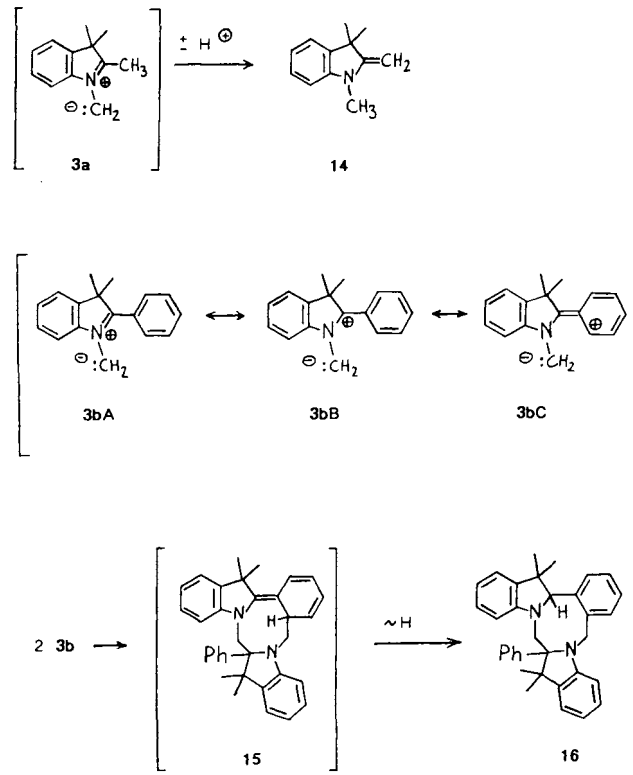
Together with the cases known from the literature[3a] these examples may serve to demonstrate that the pyrrolo-[1,2-*a*]indole skeleton may be constructed by addition of dipolarophiles to 3*H*-indolium ylides.

Generation of 3a,b in Absence of Dipolarophiles

In absence of added dipolarophiles but under otherwise the same conditions of (trimethylsilyl)methylation and desilylation, Fischer base **14** was obtained as readily identified product from **1a**, probably via **3a** by prototropy. Since this pathway may be followed also in the presence of dipolarophiles, it is remarkable that trapping products from **3a** (as **4, 7,** and **11**) are formed at all. Besides **14** a fraction of higher molecular mass is obtained, which displays peaks at m/z = 418, 346, 246 indicating a possible reaction between the starting 2,3,3-trimethyl-1[(trimethylsilyl)methyl]-3*H*-indolium ion with **14** and not necessarily the formation of a true dimer of **3a**.

1b, however, when treated as **1a** in the absence of dipolarophiles, was transformed into an unsymmetrical dimer of

Scheme 2



3b. Structure **16** assigned to this dimer is derived from its spectral data as follows: The 70-eV EI-mass spectrum (M^+ at *m/z* 470) does not show a fragment corresponding to one half of its molecular mass but the parent peak at *m/z* = 249 corresponding to a fragment containing both methylene groups. The 80-MHz ^{1}H-NMR spectrum shows a singlet for 10b-H at δ = 3.83 ppm and two AB quartets for the protons at C-17 (δ_A = 3.80, δ_B = 3.41, $|J_{AB}|$ = 13.9 Hz) and at C-6 (δ_A = 4.80, δ_B = 4.62, $|J_{AB}|$ = 17.6 Hz).

The formation of the eight-membered ring may be explained by delocalization of the positive charge away from C-2 (resonance formula **3bB**) into the 2-phenyl ring (resonance formula **3bC**) and addition of the formal 1,5-dipole **3bC** to the familiar 1,3-dipole (**3bA** or **3bB**), which would formally constitute a thermally allowed (6π + 4π) cycloaddition[8] forming the (unstable) precursor **15**. The latter in turn undergoes a formal 1,3-hydrogen shift to generate **16**. We have, however, no indications whatsoever on the nature of these processes (stepwise or concerted). Acceptor-substituted isoquinolinium and phthalazinium ylides do form symmetric dimers with a central piperazine ring[9].

Investigations aimed at elucidation of the regioselectivity of the cycloadditions of 3*H*-indolium ylides are in progress.

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Experimental

All melting points and boiling points are uncorrected. In case of kugelrohr distillations (KD) the oven temperatures are given. – ^{1}H-NMR spectra: Varian EM 360 (60 MHz) or Bruker WP 80 (80 MHz) and WM 300 (300 MHz). – IR spectra: Perkin-Elmer 397 and 283 instruments. – Mass spectra (70 eV, EI mode, temperature of inlet system given): MAT 311 A spectrometer. – Elemental analyses: Carlo Erba 1106 CHN analyzer. – 1,2-Dimethoxyethane (DME, b.p. 84°C) and other solvents were dried by standard procedures. – Preparative Layer Chromatography (PLC): Glass plates 48 × 20 cm, 1-mm layer of an aqueous paste of silica gel Merck PF_{254}, either used air-dry or after activation at 120°C. 5 Plates were taken for each separation and unless specified otherwise, toluene/ethyl acetate (Tol/EA) mixtures were used for development of chromatograms. Zones detected by quenching of the indicator fluorescence were excarved and eluted with acetone or ethyl acetate. The residue was subjected to further treatment.

Generation and Trapping of Methanides **3a–d** – *General Procedure:* All operations were carried out under a stream of dry nitrogen. In a carefully dried 100-ml three-necked flask, fitted with a condenser, a gas inlet tube, and a septum, an equimolar amount of (trimethylsilyl)methyl trifluoromethanesulfonate (**2**) was added by means of a syringe to the specified amount of neat 3*H*-indole (**1a–d**) under cooling with ice/water. Gentle heating, however, was applied whenever necessary to achieve complete intermediate liquefaction followed by formation of the solid 3*H*-indolium salt. 35 ml of dry DME, the specified amount of dipolarophile (if any), and an equivalent amount of carefully dried caesium fluoride were added and the septum replaced by a stopper. The mixture was kept at the temperatures given for the times specified. Hereafter, the solvent was removed in vacuo and the residue treated with 30 ml of diethyl ether and 50 ml of saturated sodium carbonate solution. The aqueous phase was extracted with ether and the combined ether phases were dried with sodium carbonate. The residue was either subjected to KD or recrystallization. The mother liquors were always checked for other components by ^{1}H NMR.

Products from **3a**: In four separate runs, each 796-mg portion (5.0 mmol) of 2,3,3-trimethyl-3*H*-indole (**1a**, freshly distilled under nitrogen) was treated with 1181 mg (5.0 mmol) each of **2**, hereafter with 7.20 g (50 mmol) of dimethyl maleate (**5**) [or 7.20 g (50 mmol) of dimethyl fumarate (**6**) or 3.55 g (25 mmol) of dimethyl ethynedicarboxylate (**10**), or no dipolarophile at all] and finally with 760 mg (5.0 mmol) of CsF. Hereafter the mixture was heated to reflux for 14 h.

Dimethyl 2,3,9,9a-Tetrahydro-9,9,9a-trimethyl-1H-pyrrolo[1,2-a]indole-1,2-dicarboxylate (**4A,B** *from* **1a** *and* **4**): Excessive **4** (together with some **14**) was removed in vacuo. PLC of the residue (Tol/EA 5:1) gave three minor zones (which contained mg quantities of material and were therefore discarded) and one major zone, the residue of which by KD (200°C, 0.01 mbar) gave 1142 mg (72%) of an oil. – IR (film): ν = 1738 cm^{-1} (C=O), 1200 (ester C–O). – 300 MHz ^{1}H NMR ($CDCl_3$): *Major isomer* **4A**: δ = 1.14, 1.37, and 1.44 (3 s, 3H each, CH_3), 3.61, 3.64 (2 s, 3H each, OCH_3), 3.11 (m_c, 2H), 3.57–3.90 (m, 2H), 6.64–7.18 (m, 4H, aromatic H). – Additional singlets present were assigned to the *minor isomer* **4B**: δ = 1.30, 1.42 (CH_3), 3.55 and 3.68 (OCH_3). From the ratio of the integrals of methyl or methoxy signals a **4A/4B** ratio of 9:1 was derived. – MS (121°C): *m/z* (%) = 317 (23, M^+), 302 (20), 286 (12), 270 (5), 258 (28), 242 (11), 226 (10), 173 (59), 158 (49), 157 (70), 128 (50), 115 (50), 113 (100), 111 (94).

$C_{18}H_{23}NO_4$ (317.4) Calcd. C 68.11 H 7.30 N 4.41
Found C 68.1 H 7.18 N 4.41

Dimethyl 2,3,9,9a-Tetrahydro-9,9,9a-trimethyl-1H-pyrrolo[1,2a]indole-1,2-dicarboxylate (**7A,B** *from* **1a** *and* **6**): The semicrystalline residue was treated with pentane, and excessive **6** was quickly separated off. The mother liquor was concentrated and treated again with a little pentane. Upon standing, colourless crystals (isomer **7A**) formed. These were dissolved in ether, the solution was filtered over silica gel to remove coloured impurities, concentrated and the residue crystallized from pentane to give 508 mg (32%) of colourless crystals, m.p. 95–97°C. – IR (KBr): ν = 1735 cm^{-1} (C=O), 1135 (ester C–O). – 300 MHz ^{1}H NMR ($CDCl_3$): δ = 1.10, 1.31, 1.48 (three s, 3H each, CH_3), 3.63, 3.72 (two s, 3H, OCH_3), 3.38–3.55 (several m, 3H), 3.69–3.87 (several m, 1H), 6.60–7.20 (several m, 4H, aromatic H). – MS (64°C): *m/z* (%) = 317 (28, M^+), 302 (10), 286 (11), 270 (14), 258 (30), 242 (30), 226 (16), 218 (8), 173 (100), 158 (90), 184 (14), 182 (10).

PLC of the mother liquor (Tol/EA 5:1) gave one intense zone, the residue of which after KD (200°C, 0.01 mbar) and crystallization from ethanol gave 680 mg (43%) of isomer **7B**, m.p. 72–74°C. – IR (KBr): ν = 1725, 1711 cm^{-1} (C=O), 1175 (C–O). – 300 MHz ^{1}H NMR ($CDCl_3$): δ = 1.13, 1.30 and 1.42 (3 s, 3H each, CH_3), 3.56 and 3.68 (2 s, 3H each, OCH_3), 3.16 (m_c, 1H), 3.44–3.93 (several m, 3H), 6.63–7.18 (m, 4H, aromatic H). – MS (64°C): *m/z* (%) = 317 (32, M^+), 302 (12), 286 (18), 270 (19), 258 (35), 242 (38), 226 (17), 210 (11), 184 (12), 182 (16), 173 (100), 158 (82).

$C_{18}H_{23}NO_4$ (317.4) Calcd. C 68.11 H 7.30 N 4.41
7A: Found C 67.94 H 7.17 N 4.38
7B: Found C 68.23 H 7.25 N 4.45

Dimethyl 9,9a-Dihydro-9,9,9a-trimethyl-3H-pyrrolo[1,2-a]indole-1,2-dicarboxylate (**11a**, from **1a** and dimethyl ethynedicarboxylate **10**): Excessive **10** (together with a some **14**) was removed by KD. PLC (Tol/EA 5:1) of the residue and KD (200°C, 0.01 mbar) of the residue of the main zone gave 1277 mg (81%) of an oil. – IR

(film): ν = 1721 cm^{-1} (C=O), 1274 (ester C–O). – 60 MHz ^1H NMR ($CDCl_3$): δ = 1.24, 1.35, and 1.55 (three s, 3H each, CH_3), 3.88 and 3.93 (two s, 3H each, OCH_3), AB (δ_A = 4.39, δ_B = 4.31, $|J_{AB}|$ = 16 Hz, CH_2-3), 6.70–7.40 (m, 4H, aromatic H). – MS (140°C): *m/z* (%) = 315 (80, M^+), 300 (49), 284 (58), 283 (100), 268 (95), 256 (66), 240 (12), 226 (30), 225 (50), 224 (40), 217 (50), 216 (25), 182 (77).

$C_{18}H_{21}NO_4$ (315.4) Calcd. C 68.55 H 6.71 N 4.44
Found C 68.02 H 6.59 N 4.37

In Absence of Dipolarophiles: KD (80–100°C, 0.001 Torr) gave 337 mg (39%) of 1,3,3-trimethyl-2-methylene-3*H*-indole (**14**, "Fischer base"), identified by comparison of its IR spectrum with that of an authentic sample[10]. The residue gave 0.30 g of a crystalline mixture (m.p. 146–148°C, from pentane) of at least 2 compounds. – MS (70 eV, 107°C): *m/z* (%) = 346 (M^+ of ylide dimer?) and 419 (M^+ of 1:1 adduct of ylide **3a** to its precursor immonium ion).

Products from **3b**: In four separate runs the following quantities were treated as given above and finally kept at reflux temperature for 14 h: a) 1106 mg (5.0 mmol) of 3,3-dimethyl-2-phenyl-3*H*-indole (**1b**, prepared[11] and purified[12] according to literature procedures, m.p. 44°C, ref.[12] 47°C), 1181 mg (5.0 mmol) of **2**, 7.2 g (50 mmol) of **4**, and 760 mg (5.0 mmol) of CsF. – b) 1106 mg (5.0 mmol) of **1b**, 1181 mg (5.0 mmol) of **2**, 3.6 g (25 mmol) of **6**, 760 mg (5.0 mmol) of CsF. – c) 553 mg (2.5 mmol) of **1b**, 591 mg (2.5 mmol) of **2**, 2.84 g (20 mmol) of **10**, 380 mg (2.5 mmol) of CsF. – d) 941 mg (4.25 mmol) of **1b**, 1063 mg (4.5 mmol) of **2**, no dipolarophile, 684 mg (4.5 mmol) of CsF.

Run a: Excessive **4** was removed in vacuo. ^1H-NMR analysis revealed that the distillate consisted of a 2:1 mixture of **4** and **6**. PLC (Tol/EA 10:1) gave three zones. The fastest moving one contained mg quantities of compound **16** (*vide infra*). The two main zones were well separated and gave one isomer each of a 1:1 adduct.

Dimethyl rel-(1R,2S,9aR)-2,3,9,9a-Tetrahydro-9,9-dimethyl-9a-phenyl-1H-pyrrolo[1,2-a]indole-1,2-dicarboxylate (**8A**): The faster moving zone gave 645 mg (34%), m.p. 116–118°C (from pentane). – IR (KBr): ν = 1732 cm^{-1} (C=O). – 300 MHz ^1H NMR ($CDCl_3$): δ = 0.56 and 1.69 (2 s, 3H each, CH_3), 3.04 and 3.54 (3 s, 3H each, OCH_3), ABX (δ_A = 3.99, δ_B = 3.79, δ_X = 2.95, $|J_{AB}|$ = 10.9, J_{AX} = 9.1, J_{BX} = 9.8 Hz) for CH_2-3 (AB) and 2-H (X), X-part showing additional coupling to 1-H ($J_{1,2}$ = 6.2 Hz), 3.55 (d, *J* = 6.2 Hz, 1H, 1-H), 6.70–7.22 (m, 4H, 5- to 8-H), 7.30–7.54 (several sharp m, 5H, 9a-phenyl). – MS (101°C): *m/z* (%) = 379 (24, M^+), 364 (2), 347 (2), 320 (10), 293 (3), 288 (6), 235 (60), 234 (100), 220 (20), 219 (10), 218 (2), 158 (18).

Dimethyl rel-(1S,2R,9aR)-2,3,9,9a-Tetrahydro-9,9-dimethyl-9a-phenyl-1H-pyrrolo[1,2-a]indole-1,2-dicarboxylate (**8B**): The second zone by KD (200°C, 0.01 mbar) gave 550 mg (29%) of an oil. – IR (film): ν = 1732 cm^{-1} (C=O), 1280 and 1202 (ester C–O). – 300 MHz ^1H NMR ($CDCl_3$): δ = 0.66 and 1.79 (2 s, 3H each, CH_3), 3.27 and 3.51 (2 s, 3H each, OCH_3), ABX (δ_A = 3.97, δ_B = 3.76, δ_X = 2.96, $|J_{AB}|$ = 12.5, J_{AX} = 6.9, J_{BX} = 11.5 Hz) for CH_2-3 (AB) and 2-H (X), X-part showing additional coupling (*J* = 10.5 Hz) with 1-H, 3.86 (d, $J_{1,2}$ = 10.5 Hz, 1H, 1-H), 6.84–7.24 (m, 4H, 5- to 8-H), 7.24–7.40 (broadened m, 5H, 9a-phenyl-H). – MS (99°C): *m/z* (%) = 379 (33, M^+), 364 (8), 348 (12), 320 (12), 293 (8), 288 (20), 235 (68), 234 (100), 220 (22), 219 (14), 218 (14), 158 (15).

Run b): rel-(1S,2S,9aR)-2,3,9,9a-Tetrahydro-9,9-dimethyl-9a-phenyl-1H-pyrrolo[1,2-a]indole-1,2-dicarboxylate (**9**): From the residue excessive **6** was sublimed off at 80°C/12 Torr. The remainder was crystallized from cyclohexane/pentane to give 1423 mg (72%) of m.p. 138–140°C. – IR (KBr): ν = 1725 cm^{-1} (C=O), 1210, 1240, 1260 (C–O). – 300 MHz ^1H NMR ($CDCl_3$): δ = 0.62 and 1.82 (2 s, 3H each, CH_3), 3.55 and 3.66 (2 s, 3H each, OCH_3), 3.50 (m_c, further split due to long range couplings, 2H, 1- and 2-H), 3.69–3.92 (m, further split due to long range couplings, 2H, CH_2-3), 6.72–7.22 (m, 4H, 5- to 8-H), 7.30–7.50 (broadened m, 9a-phenyl). – MS (70 eV, 101°C): *m/z* (%) = 379 (18, M^+), 364 (4), 348 (6), 320 (11), 293 (7), 288 (25), 235 (58), 234 (100), 220 (14), 158 (14).

$C_{23}H_{25}NO_4$ (379.5) Calcd. C 72.80 H 6.64 N 3.69
8A: Found C 73.06 H 6.51 N 3.66
8B: Found C 72.87 H 6.56 N 3.66
9: Found C 72.92 H 6.53 N 3.69

Run c): Dimethyl 9,9a-Dihydro-9,9-dimethyl-9a-phenyl-1H-pyrrolo[1,2-a]indole-1,2-dicarboxylate (**11b**): The mixture, which had assumed a deep brown colour upon addition of CsF, was concentrated, and excessive **10** was removed by bulb-to-bulb distillation. The residue was separated by PLC (Tol/EA 10:1). Minor zones containing negligible amounts of material were discarded. The residue of the main zone was subjected to KD (220°C, 0.01 mbar), the distillate gave 623 mg (66%) of pale yellow crystals, m.p. 122–124°C, (from pentane). – IR (KBr): ν = 1720 cm^{-1} (C=O). – 60 MHz ^1H NMR ($CDCl_3$): δ = 0.80 and 1.59 (two s, 3H each, CH_3), 3.67 and 3.82 (two s, 3H each, OCH_3), AB ($\delta_A \approx \delta_B \approx$ 4.35, $|J_{AB}| \approx$ 16 Hz, CH_2-3), 6.70–8.0 (m, 9H, aromatic H). – MS (118°C): *m/z* (%) = 377 (100, M^+), 346 (30), 318 (62), 300 (49), 286 (70), 268 (49), 244 (41).

$C_{23}H_{23}NO_4$ (377.4) Calcd. C 73.18 H 6.14 N 3.71
Found C 73.28 H 6.01 N 3.67

Run d): PLC (Tol/EA 10:1) of the residue obtained upon workup gave 560 mg (56%) of crystals from the most intense fast moving zone, m.p. 178–179°C (from pentane). – In an alternative run using 1106 mg (5.0 mmol) of **1b** and 1180 mg (5.0 mmol) of **2** and stirring 2 h at 85°C under argon before addition of 30 ml of DME and 1.0 g (6.6 mmol) of CsF and refluxing for 10 h, 730 mg (62%) of originally colourless crystals, m.p. 178–179°C, were obtained which assumed a red colouring after admission of air.

10b,11,17a,18-Tetrahydro-11,11,18,18-tetramethyl-17a-phenyl-6H,17H-diindolo[1,2-a:1,2-d]benzo[f][1,4]diazocine (**16**): IR (KBr): ν = 1600 cm^{-1}, 1482, 1455, 750, 738, 703. – 80 MHz ^1H NMR ($CDCl_3$): δ = 0.35, 0.54, 0.85, and 1.16 (4 s, 3H each, CH_3), AB (δ_A = 3.80, δ_B = 3.41, $|J_{AB}|$ = 13.9 Hz, CH_2-17), 3.83 (s, 1H, 5a-H), AB (δ_A = 4.80, δ_B = 4.62, $|J_{AB}|$ = 17.6 Hz, CH_2-6), 6.14–7.22 (several m, 17H, aromatic H). – MS (70 eV, 117°C): *m/z* (%) = 470 (25, M^+), 249 (100), 233 (37), 185 (20), 177 (37), 158 (65).

$C_{34}H_{34}N_2$ (470.7) Calcd. C 86.78 H 7.28 N 5.95
Found C 86.66 H 7.28 N 5.89

Products from **3c,d**

2-Methoxy-3,3-dimethyl-3H-indole (**1c**)[13]: A mixture of 2.42 g (15 mmol) of 1,3-dihydro-3,3-dimethyl-2H-indol-2-one, 3.0 g (20 mmol) of trimethyloxonium tetrafluoroborate, and 50 ml of dichloromethane was kept at room temperature for a week and the process of the alkylation was followed by TLC (Tol/EA 10:1). After concentration at room temperature the residue was taken up in 50 ml of ether, and the solution was vigorously stirred with 50 ml of saturated sodium carbonate solution. The aqueous layer was extracted five times with ether, the combined ether phases were dried with sodium carbonate, concentrated, and the residue was subjected to fractional sublimation. The product obtained in this way is still contaminated with the indolinone. Rapid KD (120°C, 0.001 mbar) gave a fraction practically pure of 2-indolinone, m.p. 60°C (ref.[13] 62°C). The residues of sublimation and KD may be recycled.

2-Ethoxy-3,3-dimethyl-3H-indole (**1d**) was prepared according to the literature[14] and purified by sublimation (0.001 Torr, 60°C), m.p. 57°C.

Dimethyl 9,9-Dimethyl-9H-pyrrolo[1,2-a]indole-1,2-dicarboxylate (**12**):

a) *From* **1c**: 700 mg (4.0 mmol) of **1c** was alkylated with 945 mg **2** following the general procedure given above with additional warming to 45–50°C for 15 min to produce a viscous oil, which was treated with 4.0 g (28 mmol) of **10** and 685 mg (4.5 mmol) of CsF. After the usual workup, excessive **10** was removed by KD (200°C, 0.01 mbar) and the residue purified by PLC (Tol/EA 5:1). The single intense zone gave 250 mg (21%, based upon used **1c**) of fluffy colourless crystals, m.p. 108–110°C (from diethyl ether).

b) *From* **1d**: To 946 mg (5.0 mmol) of **1d** was added dropwise 1180 mg (5.0 mmol) of **2** under argon, the mixture kept under argon at 80°C for 2 h, taken up with 30 ml of DME and treated first with 3.60 g (25 mmol) of **10** and hereafter with 1.0 g (6.6 mmol) of CsF. The mixture was kept at reflux temp. for 5 h. Workup and removal of excessive **10** by KD as before gave 354 mg (25%) of colourless crystals, m.p. 110–111°C (from diethyl ether). – IR (KBr): ν = 3130 cm^{-1}, 1726 (medium intense), and 1700 (very strong, C=O), 1507 (C=C), 1280, 1246, 1225 (C–O). – 60 MHz ^1H NMR ($CDCl_3$): δ = 1.66 (s, 6H, CMe_2), 3.88 and 3.91 (2 s, 3H each, OCH_3), 7.35 (m_c, 4H, aromatic H), 7.62 (s, 1H, 3-H). – MS (70 eV, 98°C): *m/z* (%) = 299 (25, M^+), 284 (12), 268 (12), 252 (100), 240 (20), 221 (21), 207 (6), 193 (10), 166 (13), 165 (12).

$C_{17}H_{17}NO_4$ (299.3) Calcd. C 68.21 H 5.72 N 4.68
Found C 68.08 H 5.71 N 4.64

1,3-Dihydro-3,3-dimethyl-1-[(trimethylsilyl)methyl]-2H-indol-2-one (**13**): The salt resulting from treatment of 946 mg (5.0 mmol) of **1d** and 1180 mg (5.0 mmol) of **2** for 48 h at 60°C under argon was worked up as given above. PLC (toluene) gave 736 mg (61%) of a pale yellow oil. – IR (film): ν = 1702 cm^{-1} (C=O). – 80 MHz ^1H NMR ($CDCl_3$): δ = 0.10 (s, 9H, $SiMe_3$), 1.36 (s, 6H, CMe_2), 3.21 (s, 2H, CH_2), 6.77–7.35 (m, 4H, aromatic H). – MS (122°C): *m/z* (%) = 247 (42, M^+), 246 (75), 232 (47), 217 (30), 146 (25), 85 (75), 83 (83), 73 (100).

$C_{14}H_{21}NOSi$ (247.4) Calcd. C 67.97 H 8.56 N 5.66
Found C 67.87 H 8.61 N 5.77

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