Oxidation of *N*-Acylindoles by Dimethyldioxirane and Singlet Oxygen: Substituent Effects on Thermally Persistent Indole Epoxides and Dioxetanes

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Received February 17, 1994®

Photooxygenation of the *N*-acylindoles **1a-d** afforded the labile indole dioxetanes **2** and the relatively stable allylic hydroperoxides **3**. The dioxetanes **2a,c,d** were sufficiently stable for isolation and spectral characterization. Additionally, they were characterized by chemical transformations, namely reduction to the indole epoxides **5** by dimethyl sulfide, acid-catalyzed rearrangement to allylic hydroperoxides **3c,d**, and thermolysis to the cleavage products **4**. Oxidation of the *N*-acylindoles **1** with dimethyldioxirane afforded the epoxides **5**, which were characterized on the basis of their spectral data and chemical transformations to the 2-indolinones **6** and 2-methyleneindoline **7**. These decomposition products (except **7e**) were fully characterized. The stability of the epoxides **5** depended on the substitution type, i.e., the carbazole epoxide **5c** decomposed already at temperatures above ca. −50 °C, whereas the cyclopentindole epoxide **5b** was stable at 20 °C for days. The latter was unequivocally characterized by X-ray analysis.

The oxidative metabolism of aromatic and heteroaromatic substrates in cells is an important pathway of their detoxification.[1] In the case of indole derivatives, dioxygenases[2] result mainly in C_2–C_3 bond scission of the pyrrole ring; singlet oxygen[3] mimics such cleavage. In the latter case, the postulated indole dioxetanes[3b] are extremly labile, presumably due to the intramolecular electron-exchange process,[4] which is initiated by electron transfer from the electron-rich lone pair of the indole nitrogen to the dioxetane functionality.[4b,c] The same applies to the photooxygenation of structurally related pyrroles, which is currently under intensive investigation.[5] Despite the extreme labile nature of dioxetanes derived from the photooxygenation of enamine-type double bonds,[6] Saito and Matsuura[3c] characterized a *N*-*tert*-butyl-substituted indole dioxetane derivative by NMR at −78 °C and by chemical transformations. In polar, protic solvents like methanol, dioxetane formation is preferred over ene reaction.[3a,7] This effect was also observed in the photooxygenation of 4,5-dihydrofurans.[7b]

On account of the electron-donating propensity of the nitrogen atom, the indole 2,3-epoxides, and quite generally enamine-type epoxides, are also quite labile substances so that only a few such α-amino-substituted epoxides could be observed to date.[5b,8,9b,d] Nonetheless, very recently it was shown[9] that *N*-acylation of indoles sufficiently deactivates the nitrogen lone pair to permit isolation and characterization of the labile indole dioxetanes **2** and epoxides **5**. The mechanistic aspects of the reaction of singlet oxygen with indoles have been well reviewed by Foote,[9a] and theoretical calculations on the cycloaddition of singlet oxygen with enamines have also been performed.[6d-f]

Presently, we report our investigation on the steric and electronic effects in the reaction of indoles **1a-d** with singlet oxygen. Additionally, the reaction of indoles **1a-e** with dimethyldioxirane to afford the corresponding epoxides **5a-e** and their thermal transformation is presented (Scheme 1). Indeed, the indole epoxide **5b** was sufficiently persistent to establish its structure rigorously by X-ray diffraction (Figure 1), to our knowledge the first crystal structure determination of an α-amido-substituted epoxide.

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® Abstract published in *Advance ACS Abstracts,* April 15, 1994.

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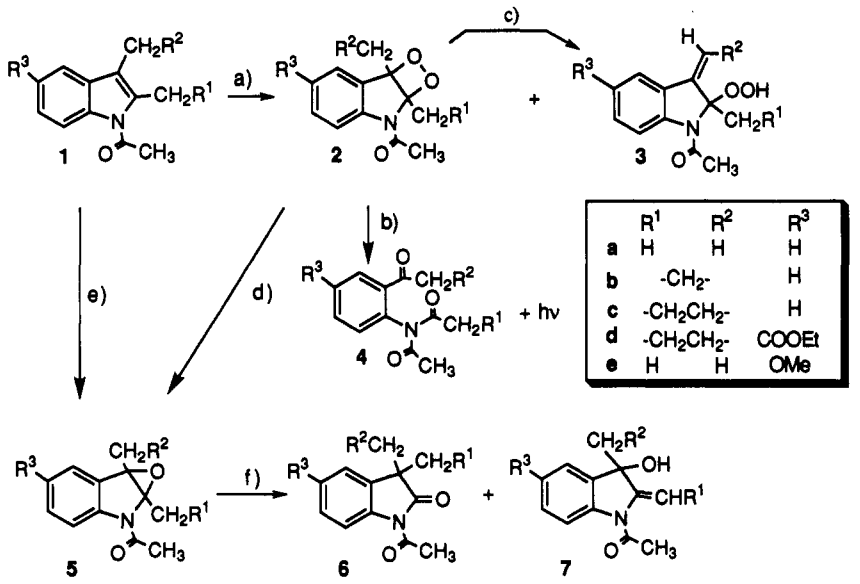
Scheme 1[a]



Key: (a) for conditions see Table 1; (b) $CDCl_3$, 20 °C, 6–12 h, yield >98%; (c) catalytic amounts of trifluoroacetic acid, $CDCl_3$, −20 °C, 1 min; (d) Me_2S (ca. 1 equiv), $CDCl_3$, −78 to −40 °C, 1–15 min, yields 67–81%; (e) dioxirane-d_6, acetone-d_6, −70 to −40 °C, 10–30 min, yield >95%; (f) acetone-d_6, 20 °C, 4–8 h, yield >95%.

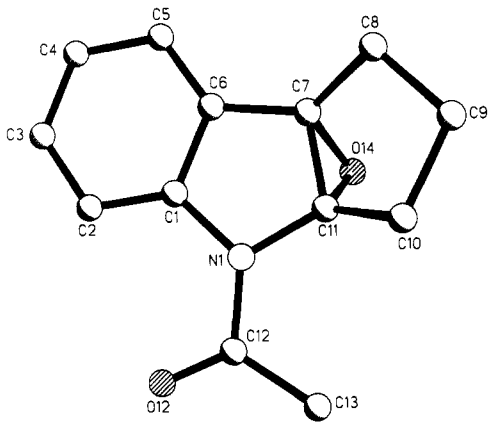


Figure 1. ORTEP drawing of the crystal structure for the epoxide **5b**.

Results and Discussion

The photooxygenation of the *N*-acylated indoles **1a-d** in dichloromethane or deuteriochloroform at subambient temperatures yielded dioxetanes **2**, allylic hydroperoxides **3**, and the C_2–C_3 cleavage products **4** (Scheme 1), most of which were isolated by low-temperature chromatography on alumina at −40 to −60 °C. Yields and conditions are given in Scheme 1. Photooxygenation of the indole **1e** was not carried out in view of its ease of autoxidation.[1b] Spectral data of the dioxetanes **2**, which are consistent with those reported,[3c,9] direct chemiluminescence, and the peroxide test (HAc/KI) confirm the peroxide structure of the labile dioxetanes **2**. The hydroperoxides **3** were stable at room temperature and, in those cases for which enough material was formed, they were isolated and fully characterized. Foote *et al.*[9a] established the regiochemistry of the ene reaction for hydroperoxide **3a** unequivocally by X-ray analysis, which is in agreement with our NOE results,[9d] so that derivatives **3b-d** were assigned by analogy of the spectral data.

The ratio of the [2 + 2] cycloadduct **2** *versus* ene product **3** depended on the substitution pattern (Table 1). These

Table 1. Ratio of [2 + 2] Cycloaddition and Ene Products in the Photooxygenation of Indoles 1a–d[a]

				ratio[b] (%)		
indole	R^1	R^2	R^3	**2 + 4**	**3**	$t_{1/2}$[c] (min)
1a	H	H	H	25:75		50 ± 0.4
1b	$-CH_2-$		H	8:92		*d*
1c	$-CH_2CH_2-$		H	90:10		14 ± 0.1
1d	$-CH_2CH_2-$		COOEt	85:15		63 ± 0.4

[a] For conditions see the Experimental Section. [b] Determined by ^1H NMR analysis (error ± 5% of stated values) directly on the crude product mixture, mass balance in all cases >90%. [c] Determined by direct chemiluminescence measurements of the isolated dioxetane **2** at 20 °C. [d] Dioxetane **2b** was not isolated due to the small amount that was formed, and thus, no kinetic data are available.

data suggest that dioxetane formation is suppressed and ene reactivity promoted in those cases (indoles **1a, b**) in which the perepoxide intermediate is stabilized by the interaction with flanking allylic hydrogen atoms[10] (Scheme 2). The electron-withdrawing ester group (indole **1d**) influences, within the NMR error limits, the product distribution only negligibly. This indicates a minor effect of the developing positive charge at C_2 (Scheme 2, path A) compared to that at C_3 (Scheme 2, path B) in the product-forming step of the dioxetane **2** from the perepoxide intermediate.

As expected, the thermal stability of the dioxetanes **2a-d** depends on the substituent. Thus, the electron-withdrawing ester group stabilizes dioxetane **2d** ($t_{1/2}$ = 63 ± 0.4 min, 20 °C) with respect to its parent derivative **2c** ($t_{1/2}$ = 14 ± 0.1 min, 20 °C). It is not surprising that **2a** ($t_{1/2}$ = 50 ± 0.4 min, 20 °C) is more stable than **2c** in view of the well-known inherent lability of six-membered, ring-annelated dioxetanes.[11] The most stable ($t_{1/2}$ = 300 min) indole 2,3-dioxetane to date, however, is the dioxetane

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Scheme 2

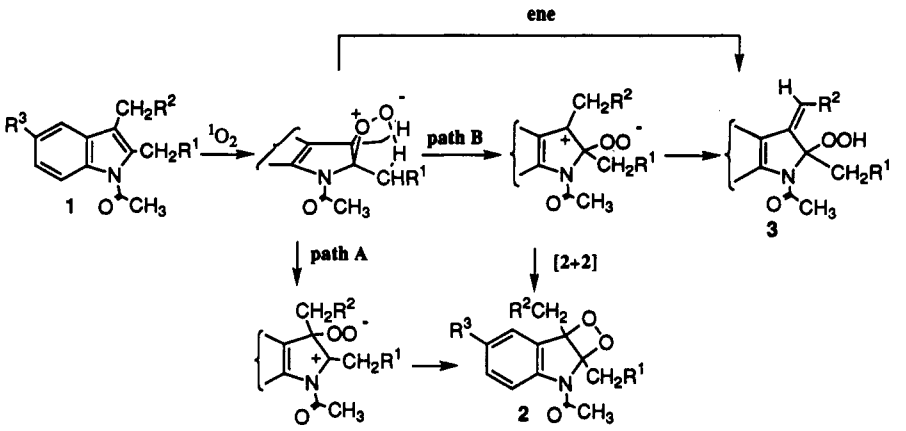


Table 2. Bond Lengths (pm) and Bond Angles (deg) of the Epoxide 5b

N(1)–C(1)	143.9(5)	C(1)–N(1)–C(11)	107.6(3)
N(1)–C(11)	144.3(5)	C(1)–N(1)–C(12)	125.4(3)
N(1)–C(12)	140.4(5)	C(11)–N(1)–C(12)	125.1(3)
C(1)–C(2)	137.3(5)	N(1)–C(1)–C(2)	129.0(4)
C(1)–C(6)	140.4(7)	N(1)–C(1)–C(6)	109.9(3)
C(2)–C(3)	139.0(8)	C(2)–C(1)–C(6)	121.1(4)
C(3)–C(4)	137.1(8)	C(1)–C(2)–C(3)	117.6(5)
C(4)–C(5)	139.3(5)	C(2)–C(3)–C(4)	121.6(4)
C(5)–C(6)	137.1(7)	C(3)–C(4)–C(5)	120.8(5)
C(6)–C(7)	149.0(5)	C(4)–C(5)–C(6)	118.1(5)
C(7)–C(8)	149.2(6)	C(1)–C(6)–C(5)	120.8(3)
C(7)–C(11)	145.5(7)	C(1)–C(6)–C(7)	107.9(4)
C(7)–O(14)	147.3(6)	C(5)–C(6)–C(7)	131.3(4)
C(8)–C(9)	154.0(7)	C(6)–C(7)–C(8)	132.1(4)
C(9)–C(10)	154.6(7)	C(6)–C(7)–C(11)	106.1(4)
C(10)–C(11)	150.9(5)	C(8)–C(7)–C(11)	110.4(3)
C(11)–O(14)	142.6(4)	C(6)–C(7)–O(14)	112.6(3)
C(12)–O(12)	120.5(5)	C(8)–C(7)–O(14)	112.6(3)
C(12)–C(13)	148.7(7)	C(11)–C(7)–O(14)	58.3(3)
		C(7)–C(8)–C(9)	103.3(4)
		C(8)–C(9)–C(10)	107.2(3)
		C(9)–C(10)–C(11)	102.2(4)
		N(1)–C(11)–C(7)	108.5(3)
		N(1)–C(11)–C(10)	127.1(3)
		C(7)–C(11)–C(10)	109.6(4)
		N(1)–C(11)–O(14)	114.0(3)
		C(7)–C(11)–O(14)	61.5(3)
		C(10)–C(11)–O(14)	115.9(3)
		N(1)–C(12)–O(12)	120.0(4)
		N(1)–C(12)–C(13)	116.6(4)
		O(12)–C(12)–C(13)	123.4(5)
		C(7)–O(14)–C(11)	60.2(3)

derived from *N*-acetyl-3-*tert*-butyl-2-methylindole.[9a] Steric stabilization by the bulky *tert*-butyl group is held responsible[3c] for the observed persistence.

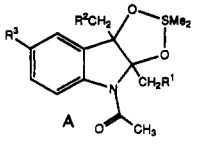
Treatment of the dioxetanes **2c,d** with catalytic amounts of trifluoroacetic acid resulted in their clean conversion to the allylic hydroperoxides **3c,d** (Scheme 1). A similar acid-catalyzed rearrangement of dioxetanes to the allylic hydroperoxides was also observed in the related benzofuran dioxetanes.[12] The spectral data of the hydroperoxides **3c,d** are identical with those observed directly in the photooxygenation of the indoles **1**. On the other hand, the thermal decomposition of the dioxetanes **2** resulted quantitatively in the C_2–C_3 cleavage products **4**, which were isolated and fully characterized. The physical data of **4c** match those reported.[13]

The reduction of the dioxetanes **2** with dimethyl sulfide at −78 °C gave the corresponding epoxides **5** (Scheme 1), as observed by NMR spectroscopy.[14] The latter were independently prepared in excellent yields by epoxidation of the indoles **1** with dimethyldioxirane[16] (Scheme 1), analogous to the recently reported direct epoxidation of indoles also by dimethyldioxirane.[9d,b] Other oxidants such as *m*-CPBA, etc. failed due to subsequent reaction with the indole epoxides.[17] The epoxide structure **5** was rigorously established by NMR spectroscopy and X-ray analysis for the persistent derivative **5b** (Figure 1).[18] The bond angles and lengths of the epoxide **5b** are given in Table 2. It is of interest to note that the C_7–O bond is 4.7 pm longer than C_{11}–O, which implies the propensity of such indole epoxides to open up preferentially at the 3-position and hence their facile 2,3-alkyl shift[8a,17d,g] to form 2-indolinones as rearrangement products. Furthermore, compared to derivative **5c**, which decomposes already above −50 °C, epoxide **5b** is stable at 20 °C for at least 2 days without noticeable decomposition, as established by NMR analysis. In analogy to epoxides **5c,d**,

(12) Adam, W.; Hadjiarapoglou, L.; Mosandl, T.; Saha-Möller, C. R.; Wild, D. *J. Am. Chem. Soc.* **1991**, *113*, 8005–8011.

(13) Ockenden, D. W.; Schofield, K. *J. Chem. Soc.* **1953**, 612–618.

(14) ^{13}C NMR spectroscopy at −78 °C exhibits two resonances in the 68–8 ppm region, which were assigned to the intermediary sulfolane **A**; further studies for its full characterization are in progress.[15] The ^{13}C NMR resonances are in agreement with those reported (Campbell, B. S.; Denny, D. B.; Denny, D. Z.; Shih, L. *J. Am. Chem. Soc.* **1975**, *97*, 3850–3851) for an analogous sulfolane.



Structure A

(15) Reinhardt, D. Diplomarbeit, Universität Würzburg, 1993.

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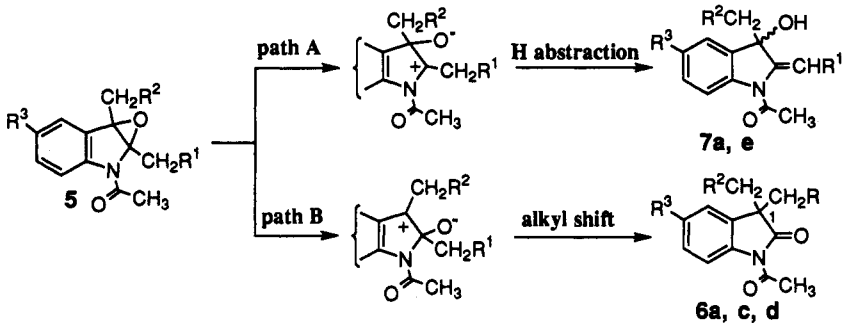
(18) Further details of the crystal structure for indole epoxide **5b** are available from the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-Technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Germany, by quoting the depository number (CSD-400617), the names of the authors, and the journal citation. The atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Scheme 3



which rearrange to the spiro-substituted 2-indolinones **6** (*vide infra*), such a transformation is energetically unfavorable since a spirocyclobutane **6b** would result on thermolysis.[19]

Thermolysis of the indole epoxides **5** led to the 2-indolinones **6** and/or 2-methyleneindoline **7** (Scheme 1). Thus, thermolysis of the 2,3-dimethylindole epoxide **5a** gave as main product indolinone **6a** and 3% indoline **7a**,[20] while the methoxy-substituted derivative **5e** afforded mainly indoline **7e**. Consequently, a positive charge at the C_2 site is promoted by a methoxy group and ring-opening of the epoxide affords after proton shift the indolinine **7a,e** (Scheme 3, path A). On the other hand, from the epoxides **5c,d** the corresponding 2-indolinones **6c,d** were produced quantitatively at 20 °C. For these derivatives, the cation at C_3 is preferred through benzylic resonance (Scheme 3, path B). Proton shift to form the corresponding allylic alcohols along path B (Scheme 3), as found in the thermolysis of benzofuran epoxides,[12] was not observed.

In summary, we have shown that the substitution pattern of the indoles **1** affects the reaction mode in the photooxygenation significantly, i.e., [2 + 2] cycloaddition *versus* ene reaction. *N*-Acylation stabilizes the labile dioxetanes **2** sufficiently for isolation; additionally, these dioxetanes were characterized by chemical transformations. Furthermore, the indole epoxides **5**, prepared by dimethyldioxirane oxidation directly of the indoles, constitute the first isolated epoxides of this type (cf. X-ray structure for derivative **5b**), whose thermal persistence also strongly depends on the substituents.

Experimental Section

General Aspects. The IR spectra were recorded on a Perkin-Elmer 1420 infrared spectrophotometer. The ^1H and ^{13}C NMR spectra were measured on a Bruker AC 200 (^1H, 200 MHz; ^{13}C, 50 MHz) or Bruker AC 250 (^1H, 250 MHz; ^{13}C, 63 MHz) spectrometer with hexamethyldisiloxane and deuteriochloroform as internal standards. Elemental analyses were carried out by the Microanalytical Division of the Institute of Inorganic Chemistry, University of Würzburg. Mass spectra (EI) were obtained at 70 eV on a Finnigan MAT 8200 and MAT 90 mass spectrometer.

All melting points were taken on a Reichert Thermovar apparatus. Silica gel (63–200 mesh; Woelm) and basic aluminum oxide 90 (70–230 mesh, activity stage 2–2.5, E. Merck, Darmstadt, Germany) were used for column chromatography, and the substrate adsorbant ratio was ca. 1:50. Low-temperature chromatography was performed on columns equipped with a vacuum-jacketed cooling mantle, through which refrigerant (−70 to −20 °C) was circulated from a RL6 Lauda Cryomat. Chromatography and collection of the fractions was run under a nitrogen gas atmosphere.

TLC analysis was conducted on precoated silica gel foils Polygram SIL G/UV_{254} (40 × 80 mm) from Macherey & Nagel. Spots were identified under a UV lamp, and peroxides were additionally detected by aqueous KI/HAc spray. Chemiluminescence measurements were performend on a Mitchell-Hastings photometer, which was thermostated by a MGW Lauda Cryomat at 20 °C (temperature control ca. ±0.2 °C).

Starting Materials. The preparation of a solution of dimethyldioxirane (DMD) in acetone and dimethyldioxirane-d_6 in acetone-d_6 followed the recently improved method.[16b] The solutions of DMD were rigorously dried over molecular sieves (4 Å). The known indoles and *N*-acetylindoles **1a-c** were prepared according to the literature procedures.[21] Their physical constants were consistent with those reported in the literature.[21] **9-Acetyl-6-carboxyethyl-1,2,3,4-tetrahydrocarbazole (1d)** was obtained analogous to the literature procedure[21c] by acylation of the corresponding carbazole[21b] in 86% yield as colorless needles, mp 132–133 °C, after column chromatography [silica gel, petroleum ether/methyl *tert*-butyl ether (5:1), R_f = 0.29]. IR (KBr pellet): ν = 3020–2820 cm^{-1}, 1712, 1610, 1580, 1475, 1379, 1325, 1247, 1108, 1040, 775. ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.41 (t, J = 7.1 Hz, 3H, CH_3), 1.87 (m, 4 H), 2.68 (s, 3 H, CH_3), 2.70 (m, 2H), 2.97 (m, 2H), 4.39 (q, J = 7.1 Hz, 2 H), 7.99 (dd, J = 8.9 Hz, J = 1.6 Hz, 1 H), 8.09 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 14.4 (q, CH_3), 21.0 (t), 21.8 (t), 23.7 (t), 26.6 (t), 27.2 (q), 60.8 (t), 115.1 (d), 118.6 (s), 119.7 (d), 125.1 (s), 125.3 (d), 130.1 (s), 136.4 (s), 139.0 (s), 167.0 (s), 169.9 (s). Anal. Calcd for $C_{17}H_{19}NO_3$ (285.3): C, 71.56; H, 6.71; N, 4.91. Found: C; 71.14, H; 6.79, N; 4.62.

***N*-Acetyl-2,3-dimethyl-5-methoxyindole (1e).** In a flame-dried 50-mL, three-necked flask, equipped with two 5-mL dropping funnels, was placed at 0 °C under a nitrogen gas atmosphere a solution of 2,3-dimethyl-5-methoxyindole[21d] (1.05 g, 5.99 mmol) in 15 mL of absolute diethyl ether. At this temperature n-BuLi (4.40 mL, 7.12 mmol) in hexane was added within 1 min, the solution was stirred for 15 min, 3 mL of acetyl chloride was added dropwise, and stirring was continued for an additional 15 min. The insoluble residue was removed by filtration and the solvent removed at 20 °C/ 0.1 Torr. Recrystallization of the oil from absolute ethanol under a nitrogen gas atmosphere resulted in 472 mg (36%) of colorless needles, mp 66–69 °C, which turned rapidly brown on exposure to air. IR (CCl_4): ν = 3000–2820 cm^{-1}, 2830, 1710, 1620, 1580, 1510, 1380, 1330, 1230, 1120, 1050. ^1H NMR ($CDCl_3$, 200 MHz): δ = 2.15 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 2.65 (s, 3 H, $COCH_3$), 3.86 (s, 3 H, OCH_3), 6.82 (m, 2 H, arom H), 7.92 (d, J = 8.0 Hz, 1 H, arom H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 8.8 (q), 14.6 (q), 27.3 (q),

(19) Witkop, B. *J. Am. Chem. Soc.* **1950**, *72*, 614–620; the 9,10-dihydroxytetrahydropentindole can be heated at reflux in alcoholic potassium hydroxide without rearrangement to the spirocyclobutane derivative.

(20) Foote[9b] found 8% of **7a** in the decomposition of epoxide **5a**, which is within the error limits of the NMR analysis in agreement with our results. The sensitivity of such epoxides toward acids was also suggested by theoretical work (George, P.; Bock, C. W. Glusker, J. P. *J. Phys. Chem.* **1992**, *96*, 3702–3708); consequently, the 2-indolinones **6** may arise through rearrangement promoted by adventitious acid.

(21) (a) Borsche, W; Groth, H. *Liebigs Ann. Chem.* **1941**, *549*, 238–243. (b) Perkin, W. H.; Plant, S. G. P. *J. Chem. Soc. Trans.* **1921**, *119*, 1825–1839. (c) Takechi, H.; Machida, M.; Kanaoka, Y. *Chem. Pharm. Bull.* **1988**, *36*, 3770–3779. (d) Roth, H. J.; Lepke, P. *Arch. Pharm.* **1972**, *305*, 159–171.

(22) Dolby, L. J.; Booth, D. L. *J. Am. Chem. Soc.* **1966**, *88*, 1049–1051.

55.6 (q), 101.1 (d), 111.2 (d), 115.4 (s), 116.0 (d), 130.3 (s), 132.2 (s), 133.2 (s), 155.9 (s), 169.8 (s). MS: *m/z* 217 (M^+, 40), 175 (M^+ - 42, 100), 160 (M^+ - 57, 66), 132 (M^+ - 85, 28). HRMS: calcd for $C_{13}H_{15}NO_2$ 217.1103, obsd 217.1117.

General Procedure for the Photooxygenation of the Indoles 1a-d. Into a 15-mL test tube, equipped with gas inlet and outlet tubes, was placed a solution of 200–250 mg (0.5–1.6 mmol) of the corresponding indole 1 and ca. 5 mg of tetraphenylporphine in 5–10 mL of dichloromethane that was distilled three times from EDTA and filtered over basic alumina (activity 1). The tube, cooled by means of a methanol bath, thermostated by a KT 290 S cryostat (Colora Messtechnik GmbH), was irradiated with two Osram sodium lamps (NAV-E; 250 W) while passing through a gentle oxygen stream and dried over $CaCl_2$/indicating silica gel/P_2O_5. The reaction progress was monitored by TLC. After completion of the photooxygenation, the solution was concentrated at -20 °C/0.1 Torr and chromatographed under a nitrogen gas atmosphere at -60 to -40 °C.

The product distribution was determined directly by NMR analysis of the crude product mixture obtained from photooxygenation of 10–20 mg (0.04–0.06 mmol) of the appropriate indole 1 in 1 mL of $CDCl_3$ under the conditions mentioned above, against hexamethyldisiloxane (10.0 μL) as internal standard.

Photooxygenation of *N*-Acetyl-2,3-dimethylindole (1a). 3-Acetyl-2a,7b-dihydro-2a,7b-dimethyl-1,2-dioxetoindole (2a), *N*-Acetyl-2-hydroperoxy-3-methyleneindole (3a), and 2′-Acetyldiacetanilide (4a). Photooxygenation of 300 mg (1.60 mmol) of indole **1a** in 5 mL of dichloromethane at -30 °C for 3 h gave after column chromatography (CH_2Cl_2 as an eluent) of the crude product 42.0 mg (12%) of dioxetane **2a** as a yellow oil. TLC (CH_2Cl_2): R_f = 0.32. ^{1}H NMR ($CDCl_3$, 200 MHz, -30 °C): δ = 1.92 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 2.26 (s, 3H, $COCH_3$), 7.05–7.24 (m, 2H), 7.60 (m, 1H), 7.82 (d, *J* = 7.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 50 MHz, -30 °C): δ = 15.1 (q, CH_3), 16.9 (q, CH_3), 27.3 (q, CH_3), 94.7 (s), 117.3 (s), 119.9 (d), 126.6 (d), 127.6 (d), 130.7 (s), 134.5 (d), 141.7 (s), 169.2 (s, C=O). The half-life of thermolysis ($t_{1/2}$ = 50 ± 0.4 min) was determined by chemiluminescence at 20 °C in CH_2Cl_2. Peroxide content of 92 ± 2% was determined by iodometric titration (KI, HAc).

On changing the eluent to CH_2Cl_2/MeOH (15:1), 170 mg (51%) of the hydroperoxide **3a** was isolated as a colorless, amorphous powder, mp 133–134 °C (lit.[9a] no data). The spectral data were identical with those reported in the literature.[9a] Anal. Calcd for $C_{12}H_{13}NO_3$ (219.2): C, 65.74; H, 5.98; N, 6.39. Found: C, 65.63; H, 5.56; N, 6.83.

2′-Acetyldiacetanilide (4a), instead of isolation from the column, was obtained quantitatively as a colorless oil from the decomposition at 20 °C of 15.3 mg (0.0690 mmol) dioxetane **2a**. IR (CCl_4): ν = 3040 cm^{-1}, 2970, 2940, 1730 (C=O), 1710 (C=O), 1600 (C=C), 1370, 1300, 1250, 1210, 1020. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.19 (s, 3H, CH_3), 2.48 (s, 6H, CH_3), 7.12 (dd, $J_{3,4}$ = 7.7 Hz, $J_{3,5}$ = 1.4 Hz, 1 H, arom H), 7.49 (m_c, 2 H, arom H), 7.79 (dd, *J* = 7.5, 1.9 Hz, 1 H, arom H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 26.8 (q, CH_3), 28.7 (2 × q, CH_3), 129.2 (d), 129.9 (d), 130.7 (d), 133.1 (d), 135.9 (s), 137.5 (s), 173.1 (2 × s, C=O), 199.1 (s, C=O). In view of the ease of hydrolysis, it was not possible to obtain a satisfactory elemental analysis.

Chromatography of **4a** (neutral alumina, activity 2) with dichloromethane as eluent gave 10.7 mg (88%) of 2′-acetylacetanilide[2] as a colorless, amorphous powder, mp 73–74 °C (lit.[22] mp 74–75 °C). IR (CCl_4): ν = 3250 cm^{-1}, 3200–3100 (NH), 3060 (CH), 1685 (C=O), 1635 (NC=O), 1590, 1565 (C=C), 1510, 1435, 1155, 950. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.21 (s, 3H, CH_3), 2.63 (s, 3H, CH_3), 7.08 (t, *J* = 8.0 Hz, 1 H, arom H), 7.53 (t, *J* = 8.0 Hz, 1 H, arom H), 7.85 (dd, *J* = 8.0, 1.1 Hz, 1 H, arom H), 8.71 (dd, *J* = 8.0, 1.5 Hz, 1 H, arom H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 25.5 (q, CH_3), 28.6 (q, CH_3), 120.9 (d), 121.6 (s), 122.2 (d), 131.5 (d), 135.1 (d), 141.5 (s), 169.9 (s), 202.8 (s).

Photooxygenation of 13.7 mg (0.0730 mmol) indole **1a** for 4 h at -30 °C resulted in the products **2a**, **3a**, and **4a** in a 18:75:7 ratio (by ^{1}H NMR analysis).

Photooxygenation of N-Acetyltetrahydrocyclopentylindole (1b). *N*-Acetyl-2,3-dihydro-1*H*,3a,8b-epidioxycyclopenta[*b*]indole (2b), 1-Acetyl-2-hydroperoxycyclopent-3-en[2,3]indoline (3b), and *N*-Acetyl-1-azabenzo[7,8]cyclooctane-2,6-dione (4b).[13] Two hundred mg (0.100 mmol) of the indole **1b** was photooxygenated in 10 mL of CH_2Cl_2 for 5 h at -30 °C. On concentration of the solution at -20 °C/0.1 Torr to ca. 1 mL, 137 mg (59%) of **3b** precipitated as a colorless, amorphous powder, mp 147–148 °C dec. The solvent was removed at the above-mentioned conditions and the crude product mixture submitted to NMR analysis.

2b. TLC (CH_2Cl_2): R_f = 0.45. ^{1}H NMR ($CDCl_3$, 200 MHz, -30 °C) δ = 1.78–1.93 (m, 4H), 2.35 (m, 4 H), 2.45 (m, 1 H), 7.07 (m, 1 H), 7.32 (m, 1 H), 7.38 (m, 1 H), 8.21 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz, -30 °C): δ = 24.7, 29.5, 30.2, 33.8, 100.7 (s), 109.6 (s), 121.0 (d), 124.8 (s), 131.3 (d), 131.7 (d), 134.1 (d), 141.9 (s), 172.4 (s). In view of its thermal lability, it was not possible to obtain a satisfactory elemental analysis.

3b. IR (KBr pellet): ν = 3190–3100 cm^{-1}, 3020, 2940, 1610, 1570, 1430, 1370, 1340, 1150, 1020, 830. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.23 (s, 3 H, CH_3), 2.62 (m_c, 3 H, aliph H), 3.00 (m_c, 1 H, aliph H), 6.38 (m, 1 H, olef H), 7.14 (dd, *J* = 7.8, 1H, arom H), 7.20 (m, *J* = 7.8 Hz, 1 H, arom H), 7.42 (d, *J* = 7.8 Hz, 1 H, arom H), 8.21 (d, *J* = 7.8 Hz, 1 H, arom H), 8.75 (s, 1 H, OOH). ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 24.1 (q), 35.7 (t), 38.91(t), 90.6 (s), 109.4 (s), 117.4 (d), 121.5 (d), 123.9 (d), 125.5 (s), 128.0 (d), 129.1 (d), 144.7 (s), 170.4 (s). Anal. Calcd for $C_{13}H_{13}NO_3$ (231.3): C, 67.52; H, 5.67; N, 6.06. Found: C, 67.65; H, 5.39; N, 5.83.

Upon standing at room temperature for 12 h, the dioxetane **2b** decomposed quantitatively (by TLC) into **4b**.[13] ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.78–1.95 (m, 2 H, aliph H), 2.17 (s, 3 H, $COCH_3$), 2.40–2.65 (m, 4 H, aliph H), 7.31–7.35 (m, 2 H, arom H), 7.72 (m, 1 H, arom H), 8.17 (m, 1 H, arom H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 20.5 (t), 27.7 (t), 28.3 (q), 41.0 (t), 118.0 (d), 126.8 (d), 127.3 (d), 128.7 (d), 131.2 (s), 141.9 (s), 171.2 (s), 173.2 (s), 199.0 (s).

Photooxygenation of 11.3 mg (0.049 mmol) of indole **1b** for 6 h at -30 °C resulted in the products **2b**, **3b**, and **4b** in a 6:91:3 ratio (by ^{1}H NMR analysis).

Photooxygenation of *N*-Acetyltetrahydrocarbazole (1c). 5-Acetyl-1,2,3,4-tetrahydro-4a,9b-epidioxycarbazole (2c), 1-Acetyl-2-hydroperoxycyclohex-3-en[2,3]indoline (3c), *N*-Acetyl-1-azabenzo[8,9]cyclononane-2,7-dione (4c).[13] A 416-mg (1.56 mmol) portion of tetrahydrocarbazole **1c** was photooxygenated for 6 h at -60 °C. The conversion was ca. 50%, as determined by ^{1}H NMR analysis. Chromatography at -60 °C on alumina with dichloromethane as eluent resulted in 69.0 mg (29%) of dioxetane **2c** as a yellow oil which contained <10% of **4c** according to ^{1}H NMR spectroscopy.

2c. TLC (CH_2Cl_2): R_f = 0.26. ^{1}H NMR ($CDCl_3$, 200 MHz, -30 °C): δ = 1.78–1.93 (m, 6 H), 2.00–2.32 (m, 4 H), 2.50 (m, 1 H), 7.18 (m, 1 H), 7.28 (m, 1 H), 7.35 (m, 1 H), 8.39 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz, -30 °C): δ = 18.8 (t), 19.8 (t), 25.0 (t), 30.2 (t), 32.9 (q), 90.6 (s), 103.6 (s), 117.1 (d), 123.0 (d), 124.0 (d), 127.3 (s), 131.7 (d), 146.5 (s), 169.2 (s). The halflife of the thermolysis ($t_{1/2}$ = 14 ± 0.1 min) was determined by chemiluminescence at 20 °C in CH_2Cl_2. In view of its thermal lability, it was not possible to obtain a satisfactory elemental analysis.

3c was prepared by treatment of the above reaction mixture with 5 μL of trifluoroacetic acid for 1 min at -20 °C, subsequent washing with 2 × 5 mL of saturated, aqueous $NaHCO_3$ at 0 °C, and drying of the organic layer with $MgSO_4$. Removal of the solvent (0 °C/16 Torr) and chromatography with 15:1 CH_2Cl_2/MeOH as eluent at 0 °C gave 43.1 mg (10%) of yellow, amorphous powder: mp 132–135 °C. TLC (15:1 CH_2Cl_2/MeOH): R_f = 0.45. ^{1}H NMR ($CDCl_3$, 200 MHz, 0 °C): δ = 1.93 (m, 2H), 2.22 (s, 3H, $COCH_3$), 2.25–2.90 (m, 4H), 6.58 (s, 1H), 7.87 (d, *J* = 6.3 Hz, 1H), 7.92 (m, 1H), 8.07 (s, 1H); 8.29 (d, *J* = 6.3 Hz, 1H), 9.22 (br s, OOH, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz, 0 °C) δ = 17.8 (t), 23.7 (t), 25.5 (t), 30.9 (q), 97.7 (s, CR_3OOH), 116.2 (d), 120.1 (d), 125.9 (d), 128.3 (s), 130.4 (d), 133.8 (d), 146.6 (s), 166.3 (s), 172.1 (s). Anal. Calcd for $C_{14}H_{15}NO_3$ (245.2): C, 68.56; H, 6.16; N, 5.71. Found: C, 68.11; H, 6.32; N, 6.09.

4c. A 17.1-mg (0.0710 mmol) portion of the dioxetane **2c** in 800 μL of $CDCl_3$ was left at 20 °C for 4 h until complete decomposition. Evaporation of the solvent and recrystallization from dichloromethane/pentane of the residue yielded 15.0 mg (88%) of colorless, amorphous powder, mp 129–130 °C (lit.[13] mp 127–128 °C). TLC (CH_2Cl_2): R_f = 0.09. IR (KBr) ν = 3010 cm^{-1}, 2980, 2970, 2840, 1740, 1730, 1612, 1500, 1460, 1385, 1310, 1275,

1260, 1130. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.55 (m_c, 1 H, aliph H), 1.78 (m_c, 2 H, aliph H), 2.04 (m_c, 2 H, aliph H), 2.40 (s, 3 H, CH_3), 2.57 (m_c, 2 H, aliph H), 2.92 (m_c, 1 H, aliph H), 7.22 (d, J = 8.0 Hz, 1 H, arom H), 7.36–7.60 (m, 3 H, arom H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 25.3 (t) 25.7 (t), 26.6 (q, CH_3), 37.7 (t), 42.6 (t), 127.0 (d), 129.1 (d), 130.1 (d), 131.5 (d), 136.1 (s), 140.1 (s), 173.7 (s, C=O), 177.1 (s, C=O), 206.1 (s, C=O).

Photooxygenation of 14.2 mg (0.0670 mmol) of indole **1c** for 6 h at −40 °C gave the products **2c, 3c,** and **4c** in a 46:9:45 ratio (by ^{1}H NMR analysis).

Photooxygenation of *N*-Acetyl-6-(carboxyethyl)-1,2,3,4-tetrahydrocarbazole (1d). 5-Acetyl-8-(carboxyethyl)-1,2,3,4-tetrahydro-4a,9b-epidioxycarbazole (2d), 1-Acetyl-5-(carboxyethyl)-2-hydroperoxycyclohex-3-en[2,3]indoline (3d), and *N*-Acetyl-1-aza-3′-(carboxyethyl)benzo[7,8]cyclononane-2,6-dione (4d). Photooxygenation of 250 mg (0.876 mmol) of the carbazole **1d** in 40 mL of dichloromethane at −40 °C for 16 h and chromatography of the residue with dichloromethane/methanol (15:1) as eluent at −60 °C resulted in 58.0 mg (21%) of **2d** as yellow oil. **2d.** TLC (CH_2Cl_2): R_f = 0.14. ^{1}H NMR ($CDCl_3$, 200 MHz, −30 °C): δ = 1.38 (t, J = 7.1 Hz, 3 H, CH_3), 1.80–1.95 (m, 6 H, aliph H), 2.05–2.17 (m, 2 H, aliph H), 2.42 (s, 3 H, CH_3), 4.28 (q, J = 7.1 Hz, 2 H, CH_2), 7.75 (d, J = 7.8 Hz, 1 H), 8.00 (s, 1 H), 8.28 (d, J = 7.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 50 MHz, −30 °C): δ = 13.6 (q) 23.4, 28.6, 29.7, 34.0 (t), 24.8 (q, C-11), 60.6 (t, C-13), 96.3 (s, C-1a), 103.5 (s, C-4a), 115.5 (d), 125.5 (d), 126.4 (s), 131.9 (s), 145.7 (s), 146.0 (d), 166.2 (s, C-12), 172.3 (s, C-10). The half-life of the thermolysis ($t_{1/2}$ = 63 ± 0.4 min) was determined by chemiluminescence at 20 °C in CH_2Cl_2. In view of its thermal lability, it was not possible to obtain a satisfactory elemental analysis.

3d was prepared as reported above for **3c**. Chromatography with 15:1 CH_2Cl_2/MeOH as eluent at 0 °C gave 48.7 mg (17%) as colorless oil. TLC (CH_2Cl_2): R_f = 0.08. ^{1}H NMR ($CDCl_3$, 200 MHz, 0 °C): δ = 1.37 (t, J =7.0 Hz, 3 H, CH_3), 1.84 (m, 2 H), 2.05–2.74 (m, 7 H), 4.32 (q, J = 7.0 Hz, 2 H, CH_2), 6.44 (s, 1 H), 7.87 (d, J = 8.0 Hz, 1 H), 8.07 (s, 1 H), 8.30 (d, J = 8.0 Hz, 1 H), 9.33 (br s, OOH, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz, 0 °C): δ = 14.4 (q), 17.8 (t), 23.7 (t), 25.4 (t), 29.4 (q), 61.0 (t), 97.7 (s), 116.2 (d), 120.1 (d), 125.8 (d), 128.3 (s), 130.4 (d), 133.8 (s), 140.2 (s), 146.6 (s), 166.3 (s), 172.1 (s). Anal. Calcd for $C_{17}H_{19}NO_5$ (317.7): C, 64.27; H, 6.03; N, 4.41. Found: C, 64.23; H, 6.19; N, 4.83.

Amide **4d** was obtained by the thermolysis of 21.3 mg (0.0670 mmol) of the dioxetane **2d** in 800 μL of $CDCl_3$ at 20 °C for 8 h. Evaporation of the solvent and recrystallization of the residue from dichloromethane/pentane yielded 19.6 mg (92%) of a colorless, amorphous powder, mp 107–115 °C. TLC (CH_2Cl_2): R_f = 0.06. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.42 (t, J = 7.2 Hz, 3 H, CH_3), 1.61 (m, 1 H, aliph H), 1.83 (m, 2 H, aliph H), 2.07 (m, 2 H, aliph H), 2.50 (s, 3 H, CH_3), 2.53–2.62 (m, 2 H, aliph H), 3.04 (m_c, 1 H, aliph H), 4.42 (q, J =7.2 Hz, 2 H, CH_2), 7.38 (d, J = 10.0 Hz, 1 H, arom H), 7.90–8.25 (m, 2 H, arom H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.1 (q), 25.3 (t), 25.7 (t), 26.6 (q, CH_3), 37.7 (t), 42.6 (t), 61.7 (t), 127.0 (d), 129.1 (d), 130.1 (s), 131.5 (d), 132.2 (s), 136.1 (s), 140.1 (s), 164.7 (s), 173.7 (s, C=O), 177.1 (s, C=O), 206.1 (s, C=O). Anal. Calcd for $C_{17}H_{19}NO_5$ (317.7): C, 64.27; H, 6.03; N, 4.41. Found: C, 64.69; H, 5.88; N, 4.15.

Photooxygenation of 12.3 mg (0.0430 mmol) of **1d** for 16 h at −60 °C gave the products **2d, 3d,** and **4d** in a ratio of 41:15:45 (by ^{1}H NMR analysis).

General Procedure for the Oxidation of the Indoles 1a-e with Dimethyldioxirane-d_6. In a dry NMR tube, flushed with nitrogen gas, was placed 0.04–0.05 mmol of the corresponding indole **1** in 100 μL of CD_2Cl_2 or acetone-d_6, and 10.0 μL of hexamethyldisiloxane was added as internal standard. The tube was cooled to −80 °C, and 700–750 μL (0.05–0.06 mmol) of ca. −50 °C cold solution of 0.08 M dimethyldioxirane-d_6 was added at once. The reaction mixture was shaken once and submitted to NMR analysis. The consumption of the starting materials was complete within 5–30 min, and the mass balance was in all cases >95%.

1-Acetyl-2,3-dimethylindole 2,3-Epoxide (5a) was prepared in >95% yield (by NMR analysis) as described in the general procedure by the reaction of 10.3 mg (0.0550 mmol) of **1a** in 100 μL of $CDCl_3$ and 700 μL (0.0567mmol) of dimethyldioxirane-d_6. ^{1}H NMR (acetone-d_6, 200 MHz, −20 °C): δ = 1.78 (s, 3 H, CH_3), 2.01 (s, 3 H, CH_3), 2.51 (s, 3 H, CH_3), 7.10 (t, J = 8.0 Hz, 1 H), 7.33 (t, J = 8.2 Hz, 1 H), 7.45 (d, J = 8.0 Hz, 1 H), 7.91 (d, J = 8.2 Hz, 1 H). ^{13}C NMR (acetone-d_6, 50 MHz, −20 °C): δ = 11.9 (q), 16.3 (q), 25.7 (q), 66.5 (s), 78.1 (s), 116.4 (d), 122.6 (d), 123.5 (d), 129.2 (d), 129.7 (s), 144.4 (s), 170.8 (s). In view of its thermal lability, it was not possible to obtain a satisfactory elemental analysis.

1-Acetylcyclopent[2,3]indole 2,3-Epoxide (5b). To a solution of 100 mg (0.500 mmol) of indole **1b** in 5 mL of dichloromethane was added 6.88 mL of 0.08 M (0.550 mmol) solution of dimethyldioxirane in acetone at 0 °C. The solvent was removed at 0 °C/16 Torr and the residue recrystallized from diethyl ether to afford 105 mg (98%) of colorless plates, mp 100–101 °C. IR (CCl_4): ν = 3020 cm^{-1}, 2940, 1715 (CO), 1620, 1490, 1480, 1410, 1390, 1350, 1220, 1010, 920. ^{1}H NMR (acetone-d_6, 200 MHz): δ = 1.80–2.30 (m, 4 H), 2.31 (s, 3 H, CH_3), 2.60 (m, 2 H), 7.01 (t, J = 8.0 Hz, 1 H), 7.32 (t, J = 8.1 Hz, 1 H), 7.45 (d, J = 8.0 Hz, 1 H), 8.15 (d, J = 8.1 Hz, 1 H). ^{13}C NMR (acetone-d_6, 50 MHz): δ = 24.7 (t), 25.5 (t), 26.6 (t), 30.1 (q), 74.7 (s), 84.4(s), 118.3 (d), 123.6 (d), 125.0 (d), 127.7 (s), 129.7 (d), 148.9 (s), 170.0 (s). Anal. Calcd for $C_{13}H_{13}NO_2$ (215.3): C, 72.54; H, 6.09; N, 6.50. Found: C, 72.51; H, 6.12; N, 6.44.

X-ray Structure Determination of Epoxide 5b: Crystal Data. Empirical formula: $C_{13}H_{13}NO_2$; molecular mass 215.25; the dimensions of the unit cell were a (pm) = 1522.9(6); b (pm) = 1583.3(7); c (pm) = 895.8(3); V (pm^3) = 2160(1) × 10^6; Z = 8; d(calcd) (g × cm^3) = 1.324; crystal system, orthorhombic; space group, *Iba*2.

Data Collection: diffractometer, Siemens R3m/V; radiation, Mo Kα; monochromator, graphite; crystal size (mm), 0.3 × 0.75 × 0.1; data collection mode, Wyckoff-scan; θ range (deg), 1.75–27.5; recip. latt. segment, h = 0–19, k = 0–20, l = 0–11; number of reflns measd, 1420; number of unique reflections, 1326; 1213 independent reflections, with $F > 3\sigma(F)$; linear absorption coefficient (mm^{-1}), 0.09.

Structural Analysis and Refinement. Solution by direct-phase determination, method of refinement, full-matrix LSQ. Hydrogen positions of riding model with fixed isotopic U. The data-to-parameter ratio was 8.37; R, R_w, 0.052, 0.050; weighting scheme was $w = 1/\sigma^2(F)$; the largest difference peak was 0.24 eÅ^{-3}; the largest difference hole 0.18 eÅ^{-3}. The program that was used (Siemens SHELXTL PLUS) was run on a Micro VAX II. The results are given in Table 2 and Figure 1.

1-Acetyl-1,2,3,4-tetrahydrocarbazole 2,3-epoxide (5c) was prepared in >95% yield (by NMR analysis) as described in the general procedure by the reaction of 13.7 mg (0.0640 mmol) of the tetrahydrocarbazole **1c** in 100 μL of dichloromethane-d_2 and 750 μL (0.0610 mmol) of dimethyldioxirane-d_6 solution in acetone-d_6 at −70 °C. ^{1}H NMR (acetone-d_6, 200 MHz, −70 °C): δ = 1.52 (m, 4 H), 1.75 (m, 2 H), 2.03 (m, 2 H), 2.43 (s, 3 H, CH_3), 7.06 (t, J = 8.0 Hz, 1 H), 7.31 (t, J = 8.1 Hz, 1 H), 7.38 (d, J = 8.0 Hz, 1 H), 7.85 (d, J = 8.1 Hz, 1 H). ^{13}C NMR (acetone-d_6, 50 MHz, −70 °C): δ = 18.6 (t), 21.2 (t), 23.9 (t), 25.5 (t), 28.5 (q), 65.7 (s), 77.0 (s), 117.4 (d), 123.4 (d), 123.7 (d), 124.5 (d), 130.0 (s), 144.5 (s), 170.9 (s). In view of its thermal lability, it was not possible to obtain a satifactory elemental analysis.

1-Acetyl-5-(carboxyethyl)-1,2,3,4-tetrahydrocarbazole 2,3-epoxide (5d) was prepared in >95% yield (by NMR analysis) as described in the general procedure by the reaction of 15.7 mg (0.0550 mmol) carbazole **1d** with 700 μL (0.0567 mmol) of dimethyldioxirane-d_6 solution in acetone-d_6 at −40 °C. ^{1}H NMR (acetone-d_6, 200 MHz, −40 °C): δ = 1.34 (t, J = 7.1 Hz, 3 H), 1.41–1.73 (m, 4 H), 2.23 (m, 1 H), 2.46 (s, 3 H, CH_3), 2.50–2.67 (m, 3 H), 4.31 (q, J = 7.1 Hz, 2 H), 7.99 (m, 1 H), 8.03 (m, 1 H), 8.10 (m, 1 H). ^{13}C NMR (acetone-d_6, 50 MHz, −40 °C): δ = 14.3 (q), 18.8 (t), 21.1 (t), 22.0 (t), 23.9 (t), 25.6 (q), 61.3 (t), 65.2 (s), 77.5 (s), 117.2 (d), 119.7 (s), 125.6 (d), 131.3 (s), 132.0 (d), 147.3 (s), 165.5 (s), 171.2 (s). In view of its thermal lability, it was not possible to obtain a satifactory elemental analysis.

1-Acetyl-2,3-dimethyl-5-methoxyindole 2,3-epoxide (5e) was prepared in >90% yield (by NMR analysis) as described in the general procedure by the reaction of 11.5 mg (0.0530 mmol) methoxyindole **1e** with 700 μL (0.0567 mmol) of dimethyldioxirane-d_6 solution in acetone-d_6 at −20 °C. ^{1}H NMR (acetone-d_6, 200 MHz, -40 °C): δ = 1.78 (s, 3 H, CH_3), 1.99 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 3.80 (s, 3 H, OCH_3), 6.93 (m, 1 H), 7.13 (s, 1 H),

8.05 (d, J = 8.2 Hz, 1 H). ^{13}C NMR (acetone-d_6, 50 MHz, −40 °C): δ = 12.2 (q), 16.6 (q) 25.9 (q), 55.0 (q), 67.5 (s), 78.4 (s), 112.1 (d), 114.3 (d), 127.3 (d), 130.8 (s), 132.7 (s), 155.8 (s), 170.3 (s). In view of its thermal lability, it was not possible to obtain a satifactory elemental analysis.

Thermal Decomposition of the Epoxides 5a-e. 1-Acetyl-3,3-dimethylindolin-2-one (6a) and 1-Acetyl-3-hydroxy-3-methyl-2-methyleneindoline (7a). The epoxide **5a**, obtained in the reaction of 412 mg (2.02 mmol) of dimethylindole **1a** with 35.5 mL (2.24 mmol) of dimethyldioxirane in acetone, decomposed during solvent removal at 20 °C/16 Torr, and chromatography of the residue on basic alumina (activity 2) afforded 358 mg (72%) of **6a**[8a] as a colorless, amorphous powder and 13.4 mg (3%) colorless crystals of the allylic alcohol **7a**, mp 85–86 °C. TLC (CH_2Cl_2): R_f = 0.23. IR (CCl_4): ν = 3400–3300 cm^{-1}, 2980, 1670, 1450, 1370, 1280, 1190, 780. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.53 (s, 3 H, CH_3), 2.44 (s, 3 H, $COCH_3$), 2.90 (s, 1 H, OH), 5.12 (s, 1 H), 5.24 (s, 1 H), 6.98 (t, J = 7.8 Hz, 1 H, arom H), 7.30 (t, J = 7.8 Hz, 1 H, arom H), 7.45 (d, J = 7.8 Hz, 1 H, arom H), 8.00 (d, J = 7.8 Hz, 1 H, arom H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 25.8 (q), 27.9 (q), 76.5 (s), 96.7 (t), 118.1 (d), 122.8 (d), 124.8 (d), 130.4 (d), 135.8 (s), 142.0 (s), 154.5 (s), 169.9 (s). Anal. Calcd for $C_{12}H_{13}NO_2$ (203.1): C, 70.90; H, 6.45; N, 6.89. Found: C, 71.41; H, 6.48; N, 6.57.

1-Acetyl-3,3-dimethylindolin-2-one (6a) and 1-acetyl-3-hydroxy-3-methyl-2-methyleneindoline (7a) were formed in a ratio of 96:4 by thermolysis of a solution of 10.3 mg (0.0550 mmol) **5a** in 800 μL of CD_2Cl_2/acetone-d_6 (1:7) at 20 °C. The spectral data of **6a** matched those reported earlier.[8a]

1-Acetylspiro[cyclopentan-1,3′(3*H*)-indol]-2′(1′)-one (6c) was formed in >95% yield by allowing 14.6 mg (0.0640 mmol) of **5c** in 800 μL of dichloromethane/acetone-d_6 (1:7) to warm above −40 °C for 30 min. The spectral and physical data matched those reported earlier.[8a]

1-Acetyl-5-(carboxyethyl)spiro[cyclopentan-1,3′(3*H*)-indol]-2′(1′)-one (6d). The epoxide **5d**, obtained in the reaction of 77.2 mg (0.285 mmol) of carbazole **1d** with 5 mL (0.341 mmol) of a 0.09 M solution of dioxirane in acetone at 0 °C, decomposed during solvent removal at 20 °C/16 Torr to afford 85.8 mg (100%) of **6d** as a colorless oil. Recrystallization from diethyl ether gave 80.6 mg (94%) of a colorless, amorphous powder, mp 126–127 °C. TLC (CH_2Cl_2): R_f = 0.66. IR (CCl_4): ν = 3000–2900 cm^{-1}, 2820, 1740, 1700, 1600, 1460, 1430, 1360, 1330, 1280, 1220, 1170, 1110, 1090. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.37 (t, $J_{12,11}$ = 7.1 Hz, 3 H, 12-H), 1.80–2.05 (m 8H, 3,4-H), 2.68 (s, 3H, 10-H), 4.34 (q, $J_{11,12}$ = 7.1 Hz, 2 H, 11-H), 7.84 (d, $J_{7,9}$ = 1.8 Hz, 1 H, 7-H), 7.95 (dd, $J_{9,10}$ = 8.5 Hz, $J_{9,7}$ = 1.8 Hz, 1 H, 9-H), 8.22 (d, $J_{10,9}$ = 8.5 Hz, 1 H, 10-H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.3 (q, C-12), 26.7 (q, C-10), 26.9 (t, C-4), 40.1 (t, C-3), 53.9 (s, C-2a), 61.1 (t, C-11), 115.8 (d, C-8), 123.2 (d, C-5), 127.4 (s, C-2b), 129.9 (d, C-7), 135.7 (s, C-6), 142.5 (s, C-10a), 165.9 (s, C-2), 170.9 (s, C-9), 182.7. Anal. Calcd for $C_{17}H_{19}NO_4$ (301.3): C, 67.76; H, 6.35; N, 4.65. Found: C, 67.65; H, 6.57; N, 4.60.

1-Acetyl-3-hydroxy-5-methoxy-3-methyl-2-methyleneindoline (7e) was spectrally detected when the solution of epoxide **5e** (obtained in the above epoxidation of indole **1e**) was allowed to warm to 20 °C. On attempted isolation by chromatography, the methyleneindoline **7e** decomposed into an intractable, complex product mixture. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.53 (s, 3 H, CH_3), 2.42 (s, 3 H, $COCH_3$), 3.72 (s, 3 H, OCH_3), 5.12 (d, J = 2.1 Hz, 1 H), 5.24 (d, J = 2.1 Hz, 1 H), 6.98 (m, 2 H, arom H), 8.10 (m, 1 H, arom H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 25.7 (q), 28.8 (q), 55.8 (q), 76.7 (s), 96.6 (t), 99.1 (s), 108.1 (d), 111.4 (d), 115.6 (s), 117.9 (d), 129.7 (s), 156.0 (s), 168.3 (s).

Acknowledgment. Generous financial support by the Deutsche Forschungsgemeinschaft (SFB 172 "Molekulare Mechanismen kanzerogener Primärveränderungen") and the Fonds der Chemischen Industrie is gratefully appreciated.