containing all the other constituents. The reactions were run at 25 °C in a thermostated cell of a Beckman 24 spectrophotometer by following the decrease in the absorption at the λ_{max} of I_3^- (358 nm). All reactions were carried out with the substrate at more than 10 times the concentration of that of I_3^- and the decrease in absorbance was recorded up to 80–90% conversion. In all cases good pseudo-first-order behavior was observed.

Equilibrium Constant Determinations. The equilibrium constants were determined by measuring the optical density of a solution containing the substrate at constant concentration [(0.6–1.0) × 10^{-3} M] and CD in variable concentration in the range (0–15) × 10^{-3} M. The wavelength for measurement was that where the difference spectrum shows a maximum. These values are shown in Table IV. All determinations were carried out in the thermostated cell of a Shimadzu spectrophotometer UV 260 with a solution of CD in water at the same concentration in the blank cell to substract any contribution to the observed absorption due to CD.

Acknowledgment. This research is supported in part by the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina (CONICET) and the Consejo Provincial de Investigaciones Científicas y Tecnológicas, Córdoba, Argentina (CONICOR). A.V.V. is a gratefull recipient of a fellowship from the CONICET.

Appendix

The interaction between CD and the substrate **3** may be described as in eq 1–3, where S represents the guest. The lack of an isosbestic point in solutions containing **3** and variable concentrations of CD indicate that more than one type of complex is being formed. These type of complexes may result from a 2:1 or 1:2 interaction between the guest S and the host CD (eq 2 and 3).

$$S + CD \rightleftharpoons \underset{\mathbf{1}}{SCD} \quad K_s \tag{1}$$

$$SCD + S \rightleftharpoons \underset{\mathbf{2}}{(S)_2CD} \quad K_{2s} \tag{2}$$

$$SCD + CD \rightleftharpoons \underset{\mathbf{3}}{S(CD)_2} \quad K_{2c} \tag{3}$$

Both types of complexes 2:1 and 1:2 (guest:cyclodextrin) have been observed with other substrates.[29,30] The expression for ΔOD as a function of the equilibrium constant for the case that eq 1 and 2 hold, is given by eq 4, where [S] represents the free substrate concentration.

$$\Delta OD = \frac{\{(\epsilon_1 - \epsilon_s) + (\epsilon_2 - 2\epsilon_s)K_{2s}[S]\}\, K_s[CD][S]_o}{1 + K_s[CD](1 + 2K_{2s}[S])} \tag{4}$$

A linear dependence of $(\Delta OD)^{-1}$ vs $[CD]^{-1}$ is expected if $K_{2s}[S] < 1$ and $\epsilon_1 \approx \epsilon_2 \approx \epsilon$ since in this case eq 4 can be simplified and trasformed into an equation of the form of eq 2 (Results). Interaction of cyclodextrins with substrates in stoichiometry different to 1:1 are known in the literature, and in general the equilibrium constant for the interactions are of similar order of magnitude.[29,30] The substrate concentration used in our experiments was 10^{-3} M and K_s and K_{2s} are expected to be of the same order of magnitude of the equilibrium constants reported in Table II for the other phenols. It follows that $K_{2s}[S] < 1$. Thus from the value of the slope and intercept of plots of $(\Delta OD)^{-1}$ vs $[CD]^{-1}$, K_s can be determined and this value is reported in Table II.

On the other hand, if eq 1 and 3 hold, the expression of ΔOD as a function of CD concentration is given by eq 5, which can be transformed into an equation of the form of eq 2 (Results) only if $K_{2c}[CD] < 1$. This would imply that $K_{2c} \ll K_s$, a relationship difficult to justify. We conclude that the main two types of interactions between **3** and CD are represented by eq 1 and 2.

$$\Delta OD = \frac{(\epsilon - \epsilon_s)K_s[CD][S]_o(1 + K_{2c}[CD])}{1 + K_1[CD](1 + K_{2c}[CD])} \tag{5}$$

Registry No. **1**, 108-95-2; **1**·CD, 73621-01-9; **2**, 533-58-4; **2**·CD, 104015-41-0; **3**, 540-38-5; **3**·CD, 104015-42-1; **4**, 95-57-8; **4**·CD, 70763-75-6; **5**, 62-53-3; **5**·CD, 73621-02-0; 2-chloro-4-iodophenol, 116130-33-7; 2-chloro-6-iodophenol, 28177-52-8; *p*-iodoaniline, 540-37-4; β-cyclodextrin, 7585-39-9; *o*-iodoaniline, 615-43-0.

(29) Connors, K. A.; Pendergarst, D. D. *J. Am. Chem. Soc.* **1984**, *106*, 7607.
(30) Herkstroeter, W. G.; Martic, P. A.; Evans, T. R.; Farid, S. *J. Am. Chem. Soc.* **1986**, *108*, 3275.

Azepino[1,2-*a*]indole Synthesis from a 1,2,3,4-Tetrahydro-9(10*H*)-acridinone and Sodium Dichloroisocyanurate[1] or Singlet Oxygen

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Received February 9, 1988

Sodium dichloroisocyanurate (**4**) acts on 7-methyl-1,2,3,4-tetrahydro-9(10*H*)-acridinone (**1**) to give principally either *cis*-1,2-diol **2** or azepino[1,2-*a*]indole **3**, by suitable choice of reactant proportions. 2,3,6-Trimethyl-4-(1*H*)-quinolinone (**6**) yields a novel, methylene-bridged, oxygenated dimer **9**, while with excess **4** the chief product is the 1,2-dihydro-3*H*-indol-3-one **7**. 6-Methyl-2-phenyl-4(1*H*)-quinolinone (**12**) initially gives the 3-chloro derivative **14**, which then reacts further with **4**, yielding chlorine-free 6-methyl-2-phenyl-4*H*-3,1-benzoxazin-4-one (**16**). The sensitized photooxidation of acridinone **1** furnishes azepinoindole **3** en route to dicarboxylic acid **5**; upon similar treatment, quinolinone **6** provides the analogous indolone **7**. Reaction pathways to account for the results are presented. *N*-Halo imide **4** offers advantages over the more conventional NaOCl in synthesis as illustrated also with a "one-pot" Hofmann degradation of 4-chlorobenzamide.

Recently,[2,3] we described the oxidation of 7-methyl-1,2,3,4-tetrahydro-9(10*H*)-acridinone (**1**) with sodium hypochlorite to give, initially, *cis*-4a,9a-dihydroxy-1,2,3,4,4a,9a-hexahydro-7-methyl-9(10*H*)-acridinone (**2**)

(1) Chemical Abstracts name for sodium dichloroisocyanurate: 1,3-dichloro-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione, sodium salt. That for trichloroisocyanuric acid is 1,3,5-trichloro-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione.

(2) Boeyens, J. C. A.; Denner, L.; Marais, J. L. C.; Staskun, B. *S. Afr. J. Chem.* **1986**, *39*, 221.
(3) Boeyens, J. C. A.; Denner, L.; Marais, J. L. C.; Staskun, B. *S. Afr. J. Chem.* **1988**, *41*, 63.

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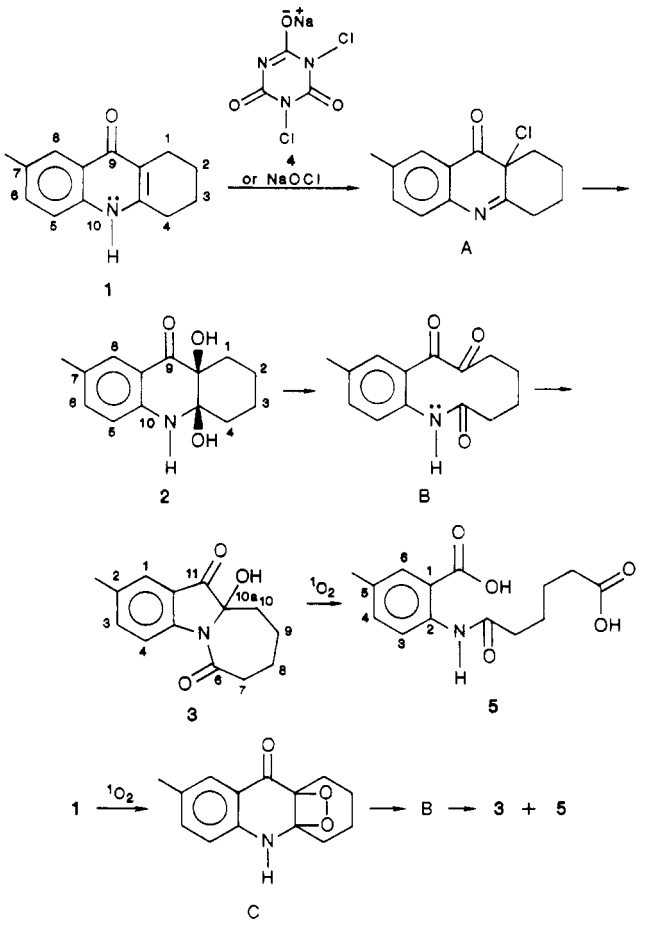
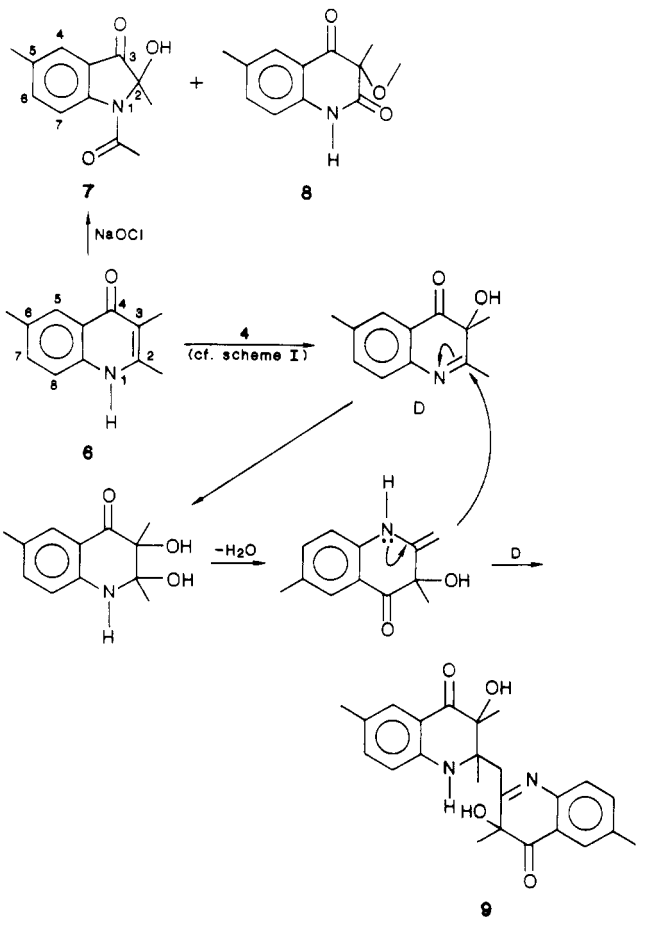
Scheme I



Scheme II



and, eventually, 7,8,9,10,10a,11-hexahydro-10a-hydroxy-2-methyl-6*H*-azepino[1,2-*a*]indole-6,11-dione (**3**). The overall reaction, 1 → **3**, is envisaged (Scheme I)[3,4] to involve several different processes, including production of an α-chloro ketone intermediate A, and culminating in the oxidation of diol **2** (via macrocycle B) to azepinoindole **3**. Because sodium hypochlorite solutions tend to deteriorate in concentration on keeping,[3,5] with alteration in molarity, product yields were variable. This disadvantage prompted us to seek a more stable and dependable oxidant furnishing the aforementioned products, in good and reproducible yields, and here we report success with the solid *N*-halo imide, sodium dichloroisocyanurate (**4**)[1], normally employed as a source of active chlorine for pool disinfection and the treatment of industrial waters.[6]

Treatment of acridinone **1** in aqueous alkali–methanol solution with a 0.5 molar proportion of **4** gave *cis*-diol **2** (61%) and minor contaminant (~10%) azepinoindole **3**. No corresponding *trans*-diol isomer was detected in the crude **2** by ^{1}H NMR, demonstrating the high stereoselectivity in this particular diol **2** synthesis. Utilization of an excess (2 molar proportions) of **4** for reaction with acridinone **1** dramatically altered the outcome, and the principal product now was nearly exclusively azepinoindole **3** (60%) and only a trace (~5%) of diol **2**. Compound **2** reacted with NaOCl[3] or with **4** to provide **3** and evidently was an important precursor for the latter in the oxidation 1 → **3**. In essence, a convenient synthesis of either diol **2** or azepinoindole **3** is now available from acridinone **1** and sodium dichloroisocyanurate (**4**) and proper choice of the reactant molar proportions. Various other solid *N*-halo imides and amides could prove to be equally effective in the above procedure; use of trichloroisocyanuric acid[1] led to azepinoindole **3** in 72% yield.

Azepinoindole **3** in alkaline solution showed considerable stability toward oxygen, but was oxidatively cleaved by singlet oxygen ($^1O_2$). Thus, whereas **3** in aqueous NaOH–methanol solution kept saturated with oxygen and irradiated with visible light for 1 h was afterward recovered (~90%) unchanged, a like solution containing Rose Bengal sensitizer after similar irradiation afforded 2-[(ω-carboxypentanoyl)amino]-5-methylbenzoic acid (**5**) (55%) (Scheme I). Hydrogen peroxide also effected the conversion of azepinoindole **3** (and of diol **2**) to acid **5**. The latter is likewise the end product in the sensitized photooxidation of acridinone **1**[7] and is hypothesized to derive via dioxetane C and a 10-membered macrocycle intermediate B (Scheme I). As B is invoked as precursor also for azepinoindole **3** (in the reaction between **1** and **4**, Scheme I), indole production in the sensitized photooxidation of **1** was sought and has now been established. Thus, reducing the period of irradiation from 90 min[7] to 20 min resulted in the isolation of azepinoindole **3** (30%) as well as acid **5** (24%); reaction for 70 min gave less of **3** and a concomitantly increased amount (43%) of **5** (Scheme I). The mechanistic aspects of this particular photochemical

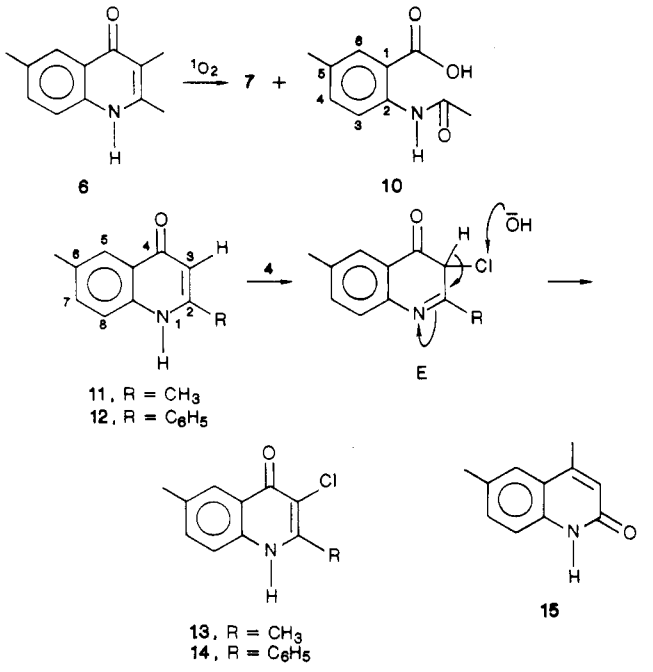
(4) Scheme I, based on Scheme I in ref 3, incorporates extensions and modifications that pertain to the current work. For the sake of simplicity, the reactant acridinones and quinolinones are portrayed as the NH compounds in the Schemes I–IV even though they undoubtedly are in the anionic form in basic solution.

(5) Stevens, R. V.; Chapman, K. T.; Weller, H. N. *J. Org. Chem.* **1980**, *45*, 2030.

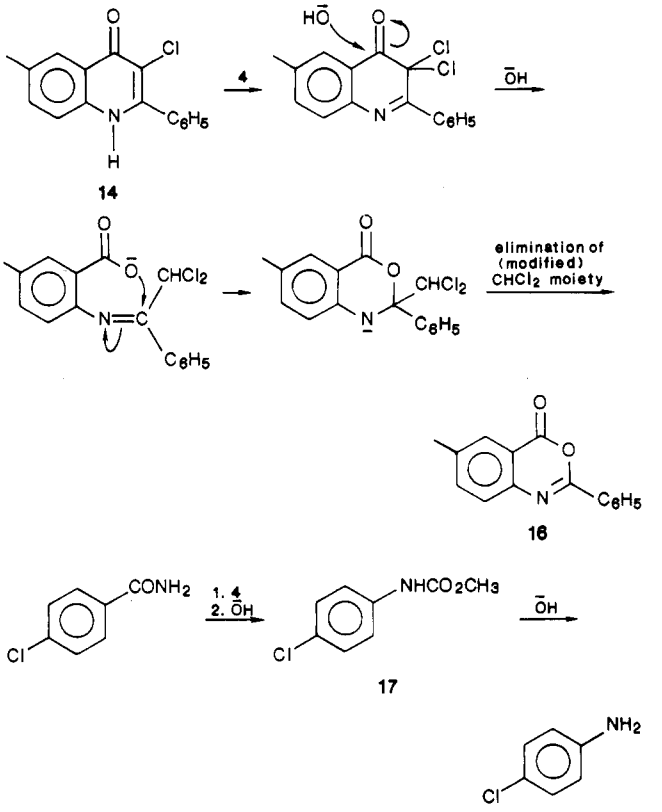
(6) *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; Wiley: New York, 1979; Vol. 7, p 407.

(7) Staskun, B.; Foote, C. S. *S. Afr. J. Chem.* **1984**, *37*, 182.

Scheme III



Scheme IV



synthesis of **3** from **1** are as yet not clarified.[8]

We turned now to the oxidation of 2,3,6-trimethyl-4-(1*H*)-quinolinone (**6**) with a molar proportion of sodium dichloroisocyanurate (**4**); previously,[3] use of NaOCl had provided 1-acetyl-1,2-dihydro-2,5-dimethyl-2-hydroxy-3*H*-indol-3-one (**7**) and a minor amount of 3,6-dimethyl-3-methoxy-2(1*H*),4(3*H*)-quinolinedione (**8**) (Scheme II). TLC monitoring of the *N*-halo imide reaction established the early production of a number of yellow, UV-fluorescent products in a mixture. One of these components (17% isolated yield) was characterized as a novel, oxygenated quinolinone dimer, of tentative structure **9** (Scheme II). This halogen-free, acid- and alkali-insoluble yellow solid had a molecular formula $C_{24}H_{26}N_2O_4$, and its IR spectrum contained absorptions for the OH, NH, and C=O functions. Particularly informative was the ^1H NMR spectrum, which showed two sets of three aromatic protons, two (aromatic) methyl singlets, three (aliphatic) methyl signals, an AB quartet for a methylene group, and three D_2O-exchangeable protons. A dimeric structure such as **9** is in keeping with the available evidence and is envisaged to result from an initially produced 3-hydroxyquinolinone intermediate D undergoing condensation with an isomeric form[9] (Scheme II). Treatment of quinolinone **6** with an excess (2 molar proportions) of reagent **4** afforded mainly indolone **7** (30%).

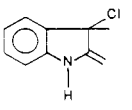
The demonstration of azepinoindole **3** formation from acridinone **1** and $^1O_2$ (vide supra) prompted us to similarly curtail the sensitized photooxidation of 4(1*H*)-quinolinone **6** (to 15 min), when indeed, the corresponding indolone **7** was isolated (20%) as well as the expected[7] 2-(acetylamino)-5-methylbenzoic acid (**10**) (Scheme III).

The study with **4** was extended to two 3-unsubstituted 4(1*H*)-quinolinones: treatment of 2,6-dimethyl-4(1*H*)-quinolinone (**11**) with a 0.55 molar amount of reagent **4** gave the 3-chloro derivative **13** (~60%), and this outcome was substantiated with 6-methyl-2-phenyl-4(1*H*)-quinolinone (**12**), which afforded 3-chloroquinolinone **14** (71%) (Scheme III). This chlorination procedure is a convenient alternative for access to these products,[10] and the envisaged reaction pathway is shown in Scheme III where intermediate E corresponds to A in the general Scheme I. In contrast, the representative 2(1*H*)-quinolinone **15** was recovered (~90%) unchanged after a similar treatment with **4**, which suggests that initial N-chlorination of this type of amide[11] is not succeeded by a 1,3-chlorine migration; alternatively, the electronic incentive for direct 3-chlorination (as appears feasible with **1** and **6**) is lacking in the non-enaminic substrate **15**.

In another development, 3-chloroquinolinone **14** ($C_{16}H_{12}ClNO$) was itself reacted with sodium dichloroisocyanurate (**4**) and gave a product mixture from which was isolated (15% yield) a colorless solid with a molecular formula $C_{15}H_{11}NO_2$, i.e., with unexpected loss of chlorine and one C atom. This substance was characterized from its spectral properties as 6-methyl-2-phenyl-4*H*-3,1-benzoxazin-4-one (**16**). This would constitute a new synthesis of **16**, and a tentative route for its production from **14** and

(8) There is currently no compelling evidence favoring macrocycle B as the necessary and immediate precursor for **3** as indicated in Scheme I. An alternative route to **3** from **2** and **4** (and from **1** and $^1O_2$), which obviates the need for B, may be envisaged: thus, an appropriate precursor, such as dioxetane C (Scheme I), may undergo a (possibly concerted) bond reorganization with concomitant ring contraction and construction of the azepinoindole **3** framework. For an analogous ring contraction, see: Hornyak, G.; Lempert, K.; Pjeczka, E.; Tôth, G. *Tetrahedron* **1985**, *41*, 2847.

(9) A related intermediate of the type



is derived from 2,3-dimethylindole and NaOCl. Gassman, P. G.; Campbell, G. A.; Mehta, G. *Tetrahedron* **1972**, *28*, 2749.

(10) Czech Pat. 135 418 (*Chem. Abstr.* **1971**, *74*, 99906*n*) halogenates the parent compounds with halo imides of dicarboxylic acids in hot acetic acid.

(11) *The Chemistry of Heterocyclic Compounds—Quinolines, Part 1*; Jones, G., Ed.; Wiley: London, 1977; p 386.

4 is outlined in Scheme IV.[12,13]

The replacement in a synthetic procedure of NaOCl by 4 (or other solid allied reagent) for improvement of yields, reproducibility of results, and convenient usage warrants further investigation. This point was illustrated by conducting a "one-pot" Hofmann degradation of 4-chlorobenzamide with 4 in aqueous NaOH–methanol solution to afford 4-chlorobenzenamine (55%) or, if required, the intermediate methyl carbamate 17 (56%) (Scheme IV).

In summary, sodium dichloroisocyanurate (4) is recommended as a reliable reagent for the preparation of *cis*-1,2-diol 2 and azepinoindole 3 from acridinone 1, and for access to a wide range of oxidation and chlorination products (indolone 7, dimer 9, 4*H*-3,1-benzoxazin-4-one 16, 3-chloroquinolinone 14) from the appropriate 4(1*H*)-quinolinone.

Experimental Section

General. Melting points were taken on a Kofler hot-stage apparatus and are uncorrected. IR spectra (KBr disk) were obtained on a Pye-Unicam SP3-300 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 200-MHz instrument in $CDCl_3$ (unless otherwise noted) with TMS as internal standard. Mass spectra were measured on a Varian MAT CH7 spectrometer at 70 eV. Column chromatography was on Merck Kieselgel 60 (70–230 mesh) with benzene–acetone (3:1, v/v) as eluent. TLC was performed on plastic plates (Merck, silica gel $60F_{254}$) with the same solvent mixture, and compounds were visualized under UV light and/or in an iodine chamber. Sodium hypochlorite reagent (15% w/v) and hydrogen peroxide (30% v/v) were SAARCHEM grade. Sodium dichloroisocyanurate (4) (Hunter Chemicals, purity 93%) and trichloroisocyanuric acid (Sigma, Italy) were used without further purification. The photooxidation apparatus and procedure were described previously.[7] No serious attempts were made to optimize yields.

***cis*-4a,9a-Dihydroxy-1,2,3,4,4a,9a-hexahydro-7-methyl-9(10*H*)-acridinone (2).** *N*-Chloro imide 4 (330 mg, 1.5 mmol) was added in one portion to a stirred solution of acridinone 1 (640 mg, 3.0 mmol) in a mixture of methanol (50 mL), 2 M sodium hydroxide (10 mL), and water (25 mL); the reagent granules gradually disappeared, and the reaction was accompanied by a mild exothermic effect. After 10 min, the stirring was discontinued and the mixture was allowed to remain at room temperature for 1 h. Methanol-insoluble isocyanuric acid derivative[14] was separated by filtration (~300 mg), and the combined alkaline filtrate and methanol washings were concentrated to ~1/3 volume by evaporation under reduced pressure. The residual liquid was cooled, and the sparingly soluble diol 2 was collected by filtration, washed with water, dried [450 mg, 61%; free of azepinoindole 3 (by TLC)], and identified from its IR and ^{1}H NMR spectra.[2] Acidification of the filtrate afforded a minor amount (20–100 mg) of alkali-soluble azepinoindole 3.

7,8,9,10,10a,11-Hexahydro-10a-hydroxy-2-methyl-6*H*-azepino[1,2-*a*]indole-6,11-dione (3) from Acridinone 1 and Sodium Dichloroisocyanurate (4). The reaction of sodium dichloroisocyanurate (4) (1.32 g, 6.0 mmol) with acridinone 1 (640 mg, 3.0 mmol) in a mixture of methanol (50 mL), 2 M sodium hydroxide (25 mL), and water (25 mL) was conducted as described for 2, for 1 h. After separation of the methanol-insoluble material (~1.2 g), the combined alkaline filtrate and methanol washings were evaporatively concentrated to ~1/3 volume. The residual liquid was cooled, filtered to remove a trace of diol 2 and/or other insoluble material, and then acidified (5 M HCl) to afford azepinoindole 3. The product was collected by filtration, washed with water, dried [440 mg, 60%; virtually free of diol 2 contaminant (TLC)], and identified from its spectral (IR, ^{1}H NMR) properties.[3] Use of trichloroisocyanuric acid (1.40 g, 6.0 mmol) in the reaction in place of 4 likewise gave azepinoindole 3 in good (530 mg, 72%) yield. The latter product (25 mg) also resulted when diol 2 (40 mg) was reacted with 4 (100 mg) in a mixture of methanol (3 mL) and 1 M NaOH (3 mL) for 1.5 h.

Oxidation of Azepinoindole 3 to Acid 5. (A) With Singlet Oxygen. A chilled (5–10 °C) solution of 3 (400 mg) and Rose Bengal (10 mg) in a mixture of methanol (90 mL) and 2 M NaOH (10 mL) contained in a photochemical reactor was kept saturated with oxygen (ca. 0.5 L h^{-1}) bubbled in from a cylinder while being irradiated with a tungsten–halogen lamp[7] for 1 h. The solution was evaporated at room temperature, and the residue was treated with 1 M NH_3 to separate sparingly soluble (unchanged) azepinoindole 3 (120 mg, identified from its IR spectrum). Acidification of the filtrate gave acid 5 (250 mg; TLC showed negligible 3 contaminant) identified from its IR and ^{1}H NMR (CD_3SOCD_3) spectra.[7] Repetition of this reaction in the absence of Rose Bengal resulted in the recovery (350 mg) of 1 M NH_3-insoluble unchanged azepinoindole 3 (identified from its IR spectrum, TLC).

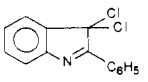
(B) With Hydrogen Peroxide. H_2O_2 (2 mL) was added to a solution of 3 (50 mg) in methanol (2 mL) and 2 M NaOH (2 mL); TLC monitoring indicated complete disappearance of 3 within 2 h. The solution was acidified (2 M HCl) and chilled when product 5 separated gradually [30 mg; identified from its IR and ^{1}H NMR spectra and chemical (1 M NH_3 soluble) properties].

Oxidation of Diol 2 to Acid 5. Hydrogen peroxide (2 mL) was added in one portion to a solution of diol 2 (50 mg) in methanol (6 mL) and water (2 mL). After 5 h, the reaction mixture was evaporatively concentrated and was then diluted with water. Product 5 was collected by filtration (38 mg; soluble in 1 M NH_3; TLC showed no diol 2 contaminant) and was identified from its IR spectrum. The oxidation of 2 in the presence of 2 M NaOH (2 mL) gave acid 5 in comparable yield. TLC monitoring of the two reactions suggested the intermediacy of azepinoindole 3 in each instance.

Photooxidation of Acridinone 1 to Azepinoindole 3. A chilled (5–10 °C) solution of acridinone 1 (500 mg) and Rose Bengal (10 mg) in a mixture of methanol (90 mL) and 2 M NaOH (10 mL) was photooxidized as described with 3, for 1 h. TLC monitoring of the reaction progress indicated a fairly rapid disappearance (within 5–10 min) of acridinone 1 and the concomitant appearance of azepinoindole 3 [as a blue fluorescent spot (366 nm)]; the latter entity itself diminished in amount with time and gave way to diacid 5. After 20 min of irradiation (when TLC showed a substantial presence of 3), the solution was evaporated at room temperature, and the residue was acidified (2 M HCl) and chilled. The product mixture (of 3 and 5) was collected by filtration and was treated with 1 M NH_3 (~10 mL) to afford sparingly soluble azepinoindole 3 (175 mg, 30%; practically free of 1 and 5, by TLC), identified from its IR and ^{1}H NMR spectra. Acidification of the ammoniacal filtrate gave diacid 5, which separated from solution as a pink (Rose Bengal contaminated) solid (160 mg, 24%; virtually free of 1 and 3, by TLC), identified from its spectral [IR, ^{1}H NMR (CD_3SOCD_3)] properties.[7] Irradiating the aforementioned solution of 1 for 1 h and 10 min resulted in less of 3 (35 mg, 6%) and more of 5 (280 mg, 43%).

Dimer 9 from Quinolinone 6 and Sodium Dichloroisocyanurate (4). Reagent 4 (1.32 g, 6.0 mmol) was added in one portion to a stirred solution of quinolinone 6[15] (1.20 g, 6.4 mmol) in a mixture of methanol (100 mL), 2 M NaOH (25 mL), and water (25 mL). After 20 min of stirring (when TLC monitoring indicated a substantial presence of several yellow products), the reaction mixture was filtered. The combined filtrate and methanol washings were acidified (with 2 M HCl, ~30 mL) and evaporatively concentrated at room temperature. The residual mass was treated with water and filtered to afford a yellow-green solid (0.9–1

(12) A related substance, viz.,



is derived from 2-phenylindole and NaOCl. De Rosa, M.; Carbognani, L.; Febres, A. *J. Org. Chem.* **1981**, *46*, 2054.

(13) The alkali-induced bond cleavage depicted for the 3,3-dichloroquinolinone in Scheme IV appears similar to that occurring in dichlorobenzoylacetanilides (Staskun, B. *J. Org. Chem.* **1974**, *39*, 3494).

(14) The identity of the methanol-insoluble (water-soluble) salt was not established.

(15) Mallams, A. K.; Israelstam, S. S. *J. Org. Chem.* **1964**, *29*, 3548.

g; TLC showed a mixture of several yellow, UV-fluorescent entities including product **9**, and with hardly any quinolinone **6**). Flash chromatography [Merck Kieselgel 60 (230–400 mesh), benzene–acetone, 10:1 (v/v)] provided a sample (~200 mg) of **9** [R_f 0.48 (benzene–acetone, 3:1)]: yellow crystals (from ethyl acetate–hexane); mp 151–153 °C; IR 3490 (sh), 3360, 3310 (OH and/or NH), 1675 (keto C=O), 1620 cm^{-1}; ^1H NMR δ 1.29 (s, 3 H, CH_3), 1.41 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 2.14 (d, J = 14 Hz, 1 H, *H*CH), 2.22 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 2.76 (d, J = 14 Hz, 1 H, HC*H*), 3.69 (s, 1 H, removed by D_2O), 4.08 (s, 1 H, removed by D_2O), 5.29 (s, 1 H, removed by D_2O), 6.38 (d, J = 8 Hz, 1 H), 6.61 (d, J = 8 Hz, 1 H), 7.1–7.2 (2 sets of dd, 2 H), 7.58 (d, J = 1 Hz, 1 H), 7.63 (d, J = 1 Hz, 1 H); MS, m/z 406 [M^+, 406.1860 ($C_{24}H_{26}N_2O_4$ requires 406.1893)], 363 (406 – 43), 345 (363 – 18), 228, 203, 188. Anal. Calcd for $C_{24}H_{26}N_2O_4$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.76; H, 6.82; N, 6.78.

Indolone 7 from Quinolinone 6 and Sodium Dichloroisocyanurate (4). The reagent **4** (1.32 g, 6.0 mmol) was added in one portion to a stirred solution of quinolinone **6** (560 mg, 3.0 mmol) in methanol (50 mL), 2 M NaOH (25 mL), and water (25 mL). After 2 h, the reaction mixture was filtered, and the combined filtrate and methanol washings were evaporatively concentrated at room temperature to ~$^1/_2$ volume. The residual solution was made just acid (5 M HCl) and chilled, when the gummy product gradually solidified. This was collected by filtration (200 mg, 30%; TLC and IR showed this to be crude indolone **7**) and purified on a column (benzene–acetone, 3:1). The 7-H broad absorption (δ 8.0) which featured in the ^1H NMR ($CDCl_3$) spectrum[3] of **7** was changed to a normal doublet (δ 8.34, J = 8 Hz) in CD_3SOCD_3 solution.

Photooxidation of Quinolinone 6 to Indolone 7. The Rose Bengal sensitized photooxidation[7] of quinolinone **6** (500 mg) was conducted as with acridinone **1**; TLC monitoring of the reaction indicated the almost complete disappearance of the substrate within 5 min, and that production of **7** initially increased and subsequently diminished with progress of the oxidation. After 15 min of irradiation, the solution was evaporated at room temperature, and the residue was acidified (2 M HCl) and chilled. Insoluble material was collected by filtration and was treated with 1 M NH_3 to effect a separation into sparingly soluble indolone **7** (115 mg, 20%) and 1 M NH_3 soluble 2-(acetylamino)benzoic acid **10** (111 mg, 21%), which were separately identified from their respective spectral (IR, ^1H NMR) properties.

Oxidation of Indolone 7 to 2-(Acetylamino)-5-methylbenzoic Acid (10). Hydrogen peroxide (1.5 mL) was added in one portion to indolone **7** (20 mg) dissolved in methanol (1.5 mL) and 2 M NaOH (1 mL); TLC monitoring showed that the reaction was completed within 15 min. The solution was evaporated at room temperature, and the residue was acidified (2 M HCl) and chilled. Crude acid **10** (9 mg, soluble in 1 M NH_3) was collected by filtration and identified from its spectral properties: IR 3300–2800, 1680, 1595 cm^{-1}; ^1H NMR (CD_3SOCD_3) δ 2.17 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 7.37 (dd, J = 2 and 8 Hz, 1 H, 4-H), 7.88 (d, J = 2 Hz, 1 H, 6-H), 8.40 (d, J = 8 Hz, 1 H, 3-H), ~11 (br s, 1 H); MS, m/z 193 (M^+), 151 (M – 42), 133 (151 – 18).

3-Chloro-2,6-dimethyl-4(1*H*)-quinolinone (13). Sodium dichloroisocyanurate (**4**) (363 mg, 1.65 mmol) was added in one portion to a stirred solution of 2,6-dimethyl-4(1*H*)-quinolinone (**11**)[15] (519 mg, 3.0 mmol) in a mixture of methanol (50 mL), 2 M NaOH (10 mL), and water (10 mL). After 40 min of stirring, the reaction mixture was filtered, and the combined filtrate and methanol washings were acidified (2 M HCl) and chilled. The solid product was collected by filtration (370 mg) and crystallized from methanol–DMF–water: colorless crystals; mp >250 °C; IR 3400–2900, 1640, 1615 cm^{-1}; ^1H NMR (CD_3SOCD_3) δ 2.41 (s, 3 H, CH_3), 2.51 (s, 3 H, CH_3), 7.4–7.5 (m, 2 H, 7-H, 8-H), 7.89 (d, J = 2 Hz, 1 H, 5-H), 12.0 (br s, 1 H, NH); MS, m/z 207 (M^+), 172 (M – 35), 144 (172 – 28).

The product was identical (IR) with **13** prepared from ethyl 2-chloroacetoacetate, 4-methylbenzenamine, and PPA.[15] Chlorination of **11** (100 mg) in methanol (10 mL), 2 M NaOH (1 mL), and water (1 mL) to **13** (~50 mg) was also effected with sodium hypochlorite (2 mL). However, 4,6-dimethyl-2(1*H*)-quinolinone[15] (**15**) (100 mg) was recovered (~90%) unchanged after treatment with **4** (100 mg) as described above, or with NaOCl (2 mL).

3-Chloro-6-methyl-2-phenyl-4(1*H*)-quinolinone (14). This was prepared from 6-methyl-2-phenyl-4(1*H*)-quinolinone[16] (**12**) (705 mg, 3.0 mmol) and **4** (363 mg, 1.65 mmol) as described for **13**. The crude product (576 mg, 71%; TLC showed only minor **12** contaminant) was crystallized from methanol–DMF–water: colorless crystals; mp >250 °C; IR 3400–2800, 1640, 1600–1550 cm^{-1}; ^1H NMR (CD_3SOCD_3) δ 2.44 (s, 3 H, CH_3), 7.5–7.7 (m, 7 H), 7.97 (d, J = 1 Hz, 1 H), 12.2 (br s, 1 H, NH); MS, m/z 269 (M^+), 234 (M – 35). Anal. Calcd for $C_{16}H_{12}ClNO$: C, 71.25; H, 4.49; N, 5.19. Found: C, 71.15; H, 4.41; N, 5.41.

6-Methyl-2-phenyl-4*H*-3,1-benzoxazin-4-one (16). Sodium dichloroisocyanurate (**4**) (1.0 g, 4.55 mmol) was added in one portion to a stirred solution of 3-chloroquinolinone **14** (1.0 g, 3.7 mmol) in a mixture of methanol (50 mL), 2 M NaOH (10 mL), and water (10 mL); a precipitate formed within minutes, giving a yellow turbid mixture, whose color deepened with time. After 90 min, the stirring was stopped, the mixture was filtered, and the yellow alkaline filtrate was acidified (2 M HCl), when crude **16** gradually separated. The latter was collected by filtration, washed with water, and dried (318 mg, 36%; TLC showed the presence of several minor contaminants). Crystallization (from methanol–water) gave (132 mg) colorless, woolly crystals: mp 114–115 °C (lit.[17] mp 140 °C); IR 1645, 1625, 1596 cm^{-1}; ^1H NMR δ 2.41 (s, 3 H, CH_3), 7.22 (d, J = 9 Hz, 1 H), 7.5–7.7 (m, 4 H), 7.86 (m, 1 H), 8.28 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.98 (CH_3), 115.41, 118.90, 122.15, 128.58, 129.98, 133.52, 134.68, 138.93, 156.58, 159.07 (2-C), 181.34 (4-C); MS, m/z 237 (M^+), 193 (M – 44), 160 (M – 77), 105 (C_6H_5CO), 77 (C_6H_5). Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.91. Found: C, 75.57; H, 4.90; N, 5.84.

Hofmann Degradation of 4-Chlorobenzamide to (i) Methyl (4-Chlorophenyl)carbamate (17) and (ii) 4-Chlorobenzenamine. (i) Reagent **4** (660 mg, 3.0 mmol) was added all at once to a stirred solution of 4-chlorobenzamide (932 mg, 6.0 mmol) in a mixture of methanol (50 mL), 2 M NaOH (15 mL), and water (30 mL). After 1 h, the reaction mixture was filtered, and the combined filtrate and methanol washings were adjusted to pH 7–8 (with 5 M HCl) and evaporated at room temperature. The residue was treated with water, and the sparingly soluble carbamate **17** was collected by filtration (617 mg, 56%; TLC and ^1H NMR showed only minor contaminants): colorless crystals (from CH_3OH–H_2O); mp 114–115 °C; IR 3270, 1660 cm^{-1}; ^1H NMR δ 3.77 (s, 3 H, CH_3), 6.6 (br s, 1 H, NH, removed by D_2O), 7.2–7.3 (m, overlapping with $CHCl_3$ signal, ca. 4 H); MS, m/z 185 (M^+).

(ii) The reaction of 4-chlorobenzamide (932 mg, 6.0 mmol) with **4** (800 mg, 3.6 mmol) was conducted as in procedure i. After neutralization, the combined filtrate and methanol washings were evaporatively concentrated to 8 mL. Following basification with 8 M NaOH (10 mL), the mixture was refluxed for 30 min, cooled, and extracted with chloroform. Evaporation of the washed and dried (Na_2SO_4) organic extract gave a residue of 4-chlorobenzenamine (420 mg, 55%; TLC showed only minor contaminants) identified by comparison (IR, ^1H NMR) with an authentic sample.

Acknowledgment. I am grateful to the Senate Research Council of the University of the Witwatersrand and to the CSIR, Pretoria, for financial support. I acknowledge the assistance of T. Sangiorgio and J. Wollbrandt with some of the experimental work and thank Dr. L. Carlton and S. Heiss for the NMR spectra.

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