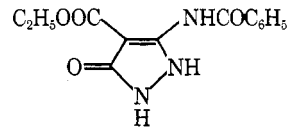
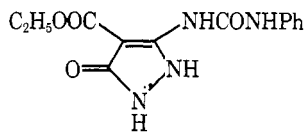


$C_{13}H_{13}N_3O_4$, 275; 260°

382 (1), 381 (5), 380 (12), 334 (2), 333 (5), 293* (380 → 334), 276 (44), 275 (76), 230 (53), //229 (47), 191* ± 1 (275 → 230, 229), 125 (18), 106 (68), 105 (100), 103 (64), 78 (27), 77 (82), 76 (16), 69 (13), 68 (67), 56.5* (275 → 125, 105 → 77), 51 (38), 50 (15), 48* (230, 229 → 106, 105), 45 (8), 44 (22), 43 (10), 41 (13), 40.2* (275 → 105), 40 (20), 39 (80), 34* (77 → 51), 31 (13), 29 (35), 27 (24)



290; 240°

290 (1.2), 289 (0.5), 275 (0.8), 245 (0.8), 229 (1.2), 199 (0.5), //172 (10), 171 (90), 125 (42), 124 (100), 120 (16), 119 (95), 91.4* (171 → 125), 91 (71), 69.7* ± 0.5 (119 → 91), 68 (90), 65 (11), 64 (40), 63 (18), 58 (11), 51 (12), 50 (10), 45* (91 → 64), 41 (14), 40 (15), 39 (17), 38 (15), 37* (125 → 68), 27 (15)

Registry No.—1 (R = Me), 22071-01-8; 1 (R = Et), 22071-11-0; 1 (R = Pr), 22071-02-9; 1 (R = Pr-*i*), 22071-03-0; 1 (R = Bu), 55254-75-6; 1 (R = Bu-*i*), 55254-76-7; 1 (R = Bu-*t*), 40764-67-8; 1 (R = Bu-*t*; R′ = Et), 51920-23-1; 3 (R = CH_3OOC), 52566-49-1; 3 (R = C_2H_5OOC), 52565-83-0; 3 (R = C_3H_7OOC), 55254-83-6; 3 (R = *i*-C_3H_7OOC), 55254-84-7; 3 (R = C_4H_9OOC), 55254-85-8; 3 (R = *i*-C_4H_9OOC), 55254-86-9; 3 (R = *t*-C_4H_9OOC), 55254-87-0; 4 (R = C_2H_5OOC), 52566-51-5; 4 (R = *n*-C_3H_7OOC), 55254-88-1; 4 (R = *i*-C_4H_9OOC), 55254-89-2; 5 (R = *n*-C_3H_7OOC), 55254-90-5; 5 (R = *i*-C_3H_7OOC), 55254-91-6; 5 (R = *i*-C_4H_9OOC), 55254-92-7; 6 (R = C_2H_5OOC), 55254-93-8; 6 (R = *n*-C_3H_7OOC), 55254-94-9; 6 (R = *i*-C_3H_7OOC), 55254-95-0; 6 (R = *i*-C_4H_9OOC), 55254-96-1; 7 (R = *n*-C_3H_7OOC), 55254-97-2; 7 (R = *i*-C_4H_9OOC), 55254-98-3; 8 (R = C_2H_5OOC), 55254-99-4; 8 (R = *n*-C_3H_7OOC), 55255-00-0; 8 (R = *i*-C_4H_9OOC), 55255-01-1; 9 (R = C_2H_5OOC), 55255-02-2; 9 (R = *n*-C_3H_7OOC), 55255-03-3; 9 (R = *i*-C_4H_9OOC), 55255-04-4; 10, (R = Et), 55255-05-5; 10 (R = Bu-*i*), 55255-06-6; hydrazine hydrate, 10217-52-4; benzoyl chloride, 98-88-4; acetyl chloride, 75-36-5; phenyl isocyanate, 103-72-0; isatoic anhydride, 118-48-9.

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Dye-Sensitized Photooxygenation of *tert*-Butylpyrroles

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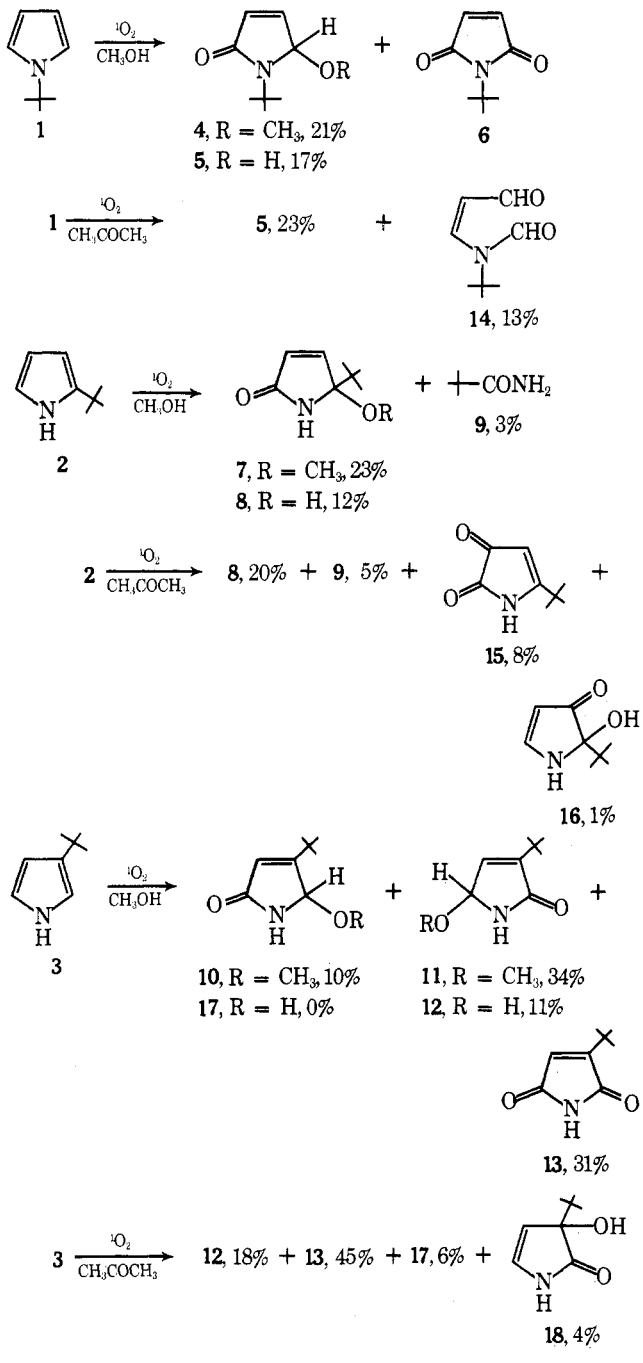
The isomeric 1,2 and 3-mono-*tert*-butylpyrroles were photooxygenated in methanol and acetone solvents using Rose Bengal and Methylene Blue singlet oxygen sensitizers. Their rates of photooxygenation are comparable to that of 2,5-dimethylfuran in methanol, but slower in acetone. Fifteen different photooxygenation products from both methanol and acetone solvents have been isolated, and their structures have been determined by spectroscopic methods. They include the expected 5-methoxy- and 5-hydroxylactams, 3-hydroxylactams, imides, pivalamide, and an unusual yellow keto lactam. The intermediate endo peroxides have been prepared at −78° and identified by low-temperature NMR.

The dye-sensitized photooxygenation of pyrroles has been the subject of recent extensive investigations,[1] especially in connection with a phototherapy method for treating neonatal jaundice due to an excess of the tetrapyrrole, bilirubin.[1,2,3] However, the first photochemical oxidation of pyrrole was reported by Ciamician and Silber in 1912:[4] photoautoxidation of pyrrole in water gave succinimide along with two unidentified crystalline compounds and a black resin. Subsequent investigations were reported by Bernheim and Morgan,[5] who found that eosin or Methylene Blue sensitized irradiation of pyrrole in water, acetone, or alcohol gave a 58% yield of an unidentified crystalline product, $C_4H_5NO_2$, mp 102.5°; and Linnel and Umar,[6] who postulated a reactive, polymerizable pyrrole endo peroxide. De Mayo and Reid[7] were the first to prove the 5-hydroxylactam structures of the products from eosin-sensitized aqueous photooxygenation of pyrrole and *N*-methylpyrrole. They accounted for their isolated photoproducts by proposing the intermediacy of an unstable endo peroxide formed by reaction of the pyrrole with singlet oxygen[8,9] [$^1O_2$] analogous to the photooxygenation of furans.[10,11] Pyrrole photooxygenations were later extended to alkylpyrroles by Lightner et al.,[1,12] and the photooxygenation of phenyl-substituted pyrroles received extensive and pioneering attention by Wasserman et al.[1,13] and Dufraisse, Rio et al.[1,14] The only reported photooxygenation study on *tert*-butylpyrroles is that of Ramasseul and Rassat,[15] who isolated hydroperoxides from 2,5-di-*tert*-butylpyrrole and 2,3,5-tri-*tert*-butylpyrrole as well as other products whose structures are reminiscent of those from 2,3,4,5-tetraphen-

Chart I



ylpyrrole.[13,16] The photooxygenation of mono-*tert*-butylpyrroles gives different products from those discussed above and are more akin to photoproducts from methyl- and ethyl-substituted pyrroles.[1]

Results

The dye-sensitized photooxygenations of 1-, 2- and 3-*tert*-butylpyrrole (**1**, **2**, and **3**) were examined in anhydrous methanol with Rose Bengal sensitizer and in anhydrous acetone with Methylene Blue sensitizer. The photoproducts (see Chart I) were isolated by column and thin layer chromatography and were characterized by a combination of spectroscopic techniques. The expected[17,18] 5-hydroxylactams (**5**, **8**, **12**) were obtained from photooxygenation in both methanol and acetone. 5-Methoxylactams (**4**, **7**, **10**, **11**) were obtained from methanol. Surprisingly high yields of 3-*tert*-butylmaleimide were found in either solvent. Unexpected new compounds including a yellow keto amide (**15**), ketol (**16**), and pivalamide (**9**) were obtained from 2-*tert*-butylpyrrole in acetone.

Table I
Reaction Rate of *tert*-Butylpyrroles with Singlet Oxygen[a]

	CH_3OH, Rose Bengal		CH_3COCH_3, Methylene Blue	
Acceptor	k_A, M^{-1} sec^{-1} (× 10^{-8})	β, M^b (× 10^3)	k_A, M^{-1} sec^{-1} (× 10^{-8})	β, M^b (× 10^3)
	1.2	0.12	0.39	0.97
	1.5	0.93	0.42	0.90
	1.8	0.78	0.30	1.3
	1.4	1.0	2.1	0.18

[a] In CH_3OH, $k_d = 1.4 \times 10^5$ sec^{-1}; in CH_3COCH_3, $k_d = 3.8 \times 10^4$ sec^{-1}; ref 19. [b] Ratio of the $^1O_2$ decay rate to the reaction rate. [c] CH_3OH values from ref 9.

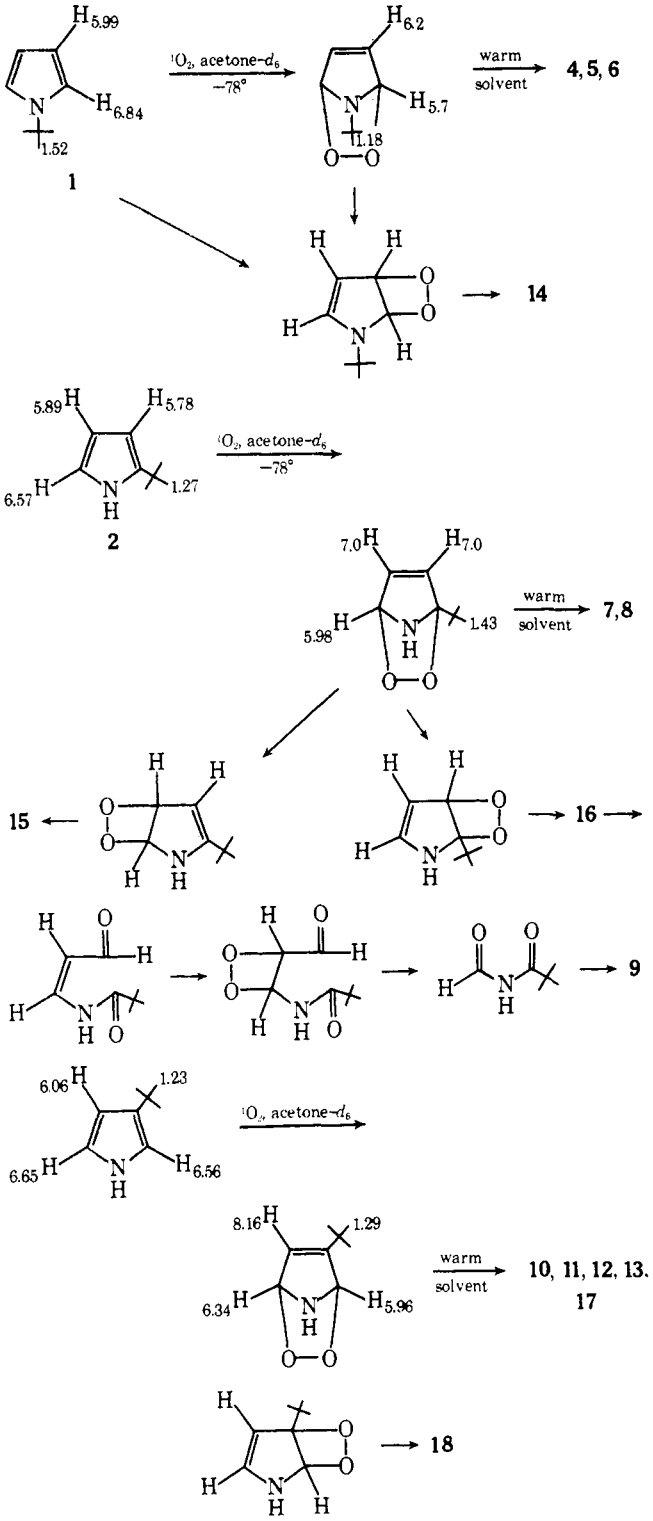
The rates of photooxygenation in methanol of the isomeric *tert*-butylpyrroles are nearly identical with each other and with that of 2,5-dimethylfuran,[9] $k_A = 1.4 \times 10^8$ M^{-1} sec^{-1}, as shown in Table I. However, the rates for the *tert*-butylpyrroles in acetone are all roughly an order of magnitude slower than that of 2,5-dimethylfuran, whose reaction rate with $^1O_2$ is slightly greater in acetone ($k_A = 2.1 \times 10^8$ M^{-1} sec^{-1}) than in methanol. Since the lifetime of $^1O_2$ is longer in acetone than in methanol,[19] the pyrrole results are surprising when contrasted to the furan behavior and are as yet unexplained.

Discussion

The origin of the majority of the photooxygenation products of the isomeric *tert*-butylpyrroles (**1–3**) can be explained by ground-state reactions of unstable endo peroxides which are formed from 1,4 addition of $^1O_2$ to the pyrrole diene system.[6,7,12] Such a mechanism is entirely analogous to that proposed in the dye-sensitized photooxygenations of furans[10,11,20] and other pyrroles,[1,7,12–18] and it readily explains the origin of the typical 2-oxo-5-alkoxy or hydroxy products. Although evidence for the formation of furan endo peroxides has been marshalled by Kane and Foote[20] in their nuclear magnetic resonance (NMR) studies at low temperatures, there have been no similar observations of pyrrole endo peroxides reported except very recently for that of *N*-phenylpyrrole.[21] In the present work we have observed the formation of the *tert*-butylpyrrole endo peroxides by NMR at −80° following dye-sensitized photooxygenation of **1**, **2**, and **3** at −78° in acetone-d_6 or Freon-11[22] (Chart II). We have also observed (NMR) their transformation upon warming to the more stable isolated photoproducts. The reactivity of the endo peroxides in methanol-*O*-*d* was too rapid at −78° to allow for their detection by NMR.

We therefore suggest that methoxylactams **4**, **7**, **10**, and **11** arise by methanolysis of their respective precursor pyrrole endo peroxides and that hydroxylactams **5**, **8**, **12**, and **17** originate either by an internal rearrangement or by adventitious hydrolysis of the same endo peroxides. Methanolysis is a well-established decomposition mechanism for furan endo peroxides[10,11,23,24] and has also been invoked frequently to explain the formation of 5-methoxylactams

Chart II



during pyrrole photooxygenation.[1,12,17,18] Too, we have established in control experiments that the methoxylactams are not formed from other photoproducts, viz., hydroxylactams, under the reaction and work-up conditions. Just how 5-hydroxylactams originate in anhydrous organic solvents, except by internal reorganization, is not clear. In a related work[25] using $H_2{}^{18}O$, the corresponding methylpyrroles were found to give hydroxylactams in methanol or acetone largely by rearrangement of the endo peroxides, and this route was still important even in water solvent. Whether the rearrangement mechanism involves sensitizer or oxygen in an H-abstraction step or whether it is entirely unimolecular has not been ascertained.

The mechanistic origin of isomeric 3-hydroxylactams (**16** and **18**) is less obvious, but they, plus **14** and **15**, might be viewed as deriving from unstable dioxetane intermediates. Whether such dioxetanes are formed directly by 1,2 addition to the pyrroles or, alternatively, by rearrangement of endo peroxides or peroxiranes[26,27] is not easy to determine. We can provide no direct evidence for either dioxetane or peroxirane precursors to the cited photoproducts, but a careful NMR examination of the *tert*-butylpyrrole photooxygenations at −78° reveals that only endo peroxides and very little else are formed in acetone-d_6 of Freon-11. Since it appears unlikely that 1,2 addition of $^1O_2$ is significant at −78°, but products from apparent 1,2 addition are observed upon warming, rearrangement of an endo peroxide to a dioxetane is presumed. In support of this, it should be noted that products presumably derived from dioxetanes generally occur in a solvent (acetone) where the endo peroxide is relatively (to methanol) long lived (cf. low-temperature NMR discussion), and apparently has time to rearrange to some extent to other reactive intermediates, e.g., dioxetanes or peroxiranes.

The ring-opened product (**14**) is a characteristic type of dioxetane cleavage product[28] which has also been found in the photooxygenation of 3,4-diethyl-2,5-dimethylpyrrole.[29] Further addition (1,2) of $^1O_2$ to the enamine-like carbon–carbon double bond[28] of **14** with subsequent cleavage of the dioxetane and hydrolysis might explain the formation of pivalamide (**9**) (Chart II). While it is clear that both **9** and **14** are just the types one expects from thermal reaction of dioxetanes[26] derived from enamines,[28,29] the origin of **15** is less obvious. Its unusual α-keto amide structure is unlike that of any pyrrole photooxidation product identified previously,[1] and we can offer no reasonable explanation for its formation other than by oxidation (H· loss or abstraction) of a precursor dioxetane (Chart II) or by oxidation of the as yet not isolated 5-*tert*-butyl-3-hydroxy-Δ^4-pyrrolin-2-one.

An isomer (**18**) of the latter has been isolated in this work, and there is ample precedent for expecting a product of this type from a 3-substituted pyrrole.[30–32] On the other hand, the 2-hydroxy-3-oxo structure of **16** is an unreported photooxygenation structure type which we have observed only once previously, with 2,3,5-trimethylpyrrole.[33] However, whether either structure type is derived from an unstable dioxetane precursor is unclear, for α-hydroxy carbonyl compounds are usually not found among the typical dioxetane decomposition structures, cf. **14**. Rather, such structures are more akin to those derived apparently from peroxiranes.[26] In either case, as noted earlier, we have found no direct evidence for dioxetane or peroxirane intermediates and speculate that should they be involved they might likely be formed from observable (NMR) endo peroxides.

The formation of maleimides, e.g., **6** and **13**, has been observed occasionally in pyrrole photooxygenations,[12,18,28–30,34] and especially in cases in which the pyrrole β positions were substituted with one or two alkyl groups. We believe that the failure to isolate maleimides from other alkylpyrroles may be due in part to the reactivity of the unsubstituted maleimide toward $^1O_2$, or its sensitivity to pH during the photooxygenation. For example, we have isolated maleimide in up to 8% yield under favorable conditions in the photooxygenation of pyrrole in methanol, but it has also been shown to undergo photooxygenation under the reaction conditions.[35] However, when a trace of ammonia is present during the photooxygenation, we can no longer isolate maleimide. Maleimides **6** and **13** may be viewed as arising from endo peroxides (Chart II) by H· loss or H· abstraction by sensitizer or oxygen.

Summary

Direct NMR evidence for endo peroxide intermediates in the photooxygenation of 1-, 2-, and 3-*tert*-butylpyrroles (1–3) has been provided. The rate of photooxygenation is faster in methanol by roughly an order of magnitude over acetone solvent. From the differing product distribution and structures, the NMR study, and the observation that the endo peroxides are longer lived in acetone than in methanol, we believe that pyrrole endo peroxides may rearrange to dioxetanes or peroxiranes when given sufficient time, and these may rearrange to a different set of products than those derived directly from endo peroxides.

Experimental Section

General. Melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. Nuclear magnetic resonance spectra were determined in $CDCl_3$ solution, unless otherwise specified, on Varian EM-360, XL-100, or a Jeolco 4H-100 spectrometers; chemical shift data are reported in parts per million downfield from internal tetramethylsilane (δ scale). Mass spectra were measured on a Varian MAT 311 or AEI MS-9 mass spectrometer. Infrared spectra were run on a Perkin-Elmer Model 457 spectrometer. Gas–liquid chromatography (GLC) was performed on a Varian Aerograph Model 1200 chromatograph with flame ionization detector, using a 6 ft × 0.125 in. aluminum 5% SE-30 on AWS Chromosorb W column with nitrogen as the carrier gas. The silica gel used for column chromatography is from M. Woelm, Eschwege 70–325 mesh ASTM and for thin layer chromatography is silica gel F, M. Woelm Eschwege. The preparative thin layer chromatography plates were 1 mm thick in adsorbent, whereas the analytical plates were 0.125 mm thin.

The methanol and acetone used were Baker Analyzed anhydrous reagent grade solvents. Pyrrole and 2,5-dimethoxytetrahydrofuran were obtained from Aldrich. Hexane-2,5-dione and Rose Bengal were obtained from Matheson, and Methylene Blue was obtained from Allied Chemical.

Synthesis of *N*-*tert*-Butylpyrrole (1). The pyrrole was prepared by the method of Josey[36] by using 2,5-dimethoxytetrahydrofuran and substituting *tert*-butylamine for methyl anthranilate. The yield of distilled product was 35%, bp 68° (30 Torr) [lit.[37] bp 74–79° (42 Torr)], as a colorless liquid which was greater than 99% pure by GLC: NMR δ 1.52 (s, 9 H, CH_3), 6.06 (m, 2 H, C=CHCH=C), 6.73 ppm (m, 2 H, C=CHN).

Synthesis of 2- and 3-*tert*-Butylpyrrole (2 and 3). These pyrroles were prepared by the method of Skell and Bean[38] and using pyrrole Grignard and *tert*-butyl chloride. The pyrroles were separated by repeated distillation through a spinning band column under partial vacuum to yield 2-*tert*-butylpyrrole, bp 78° (20 Torr), mp 44–46° [lit.[38] bp 89° (30 Torr)], and 3-*tert*-butylpyrrole, bp 93° (30 Torr) [lit.[38] bp 94° (30 Torr)]. The purity of each compound was greater than 99% by GLC. 2-*tert*-Butylpyrrole: NMR δ 1.27 (s, 9 H, $-CH_3$), 5.87 (m, 1 H, =CH), 6.03 (m, 1 H, =CH), 6.65 (m, 1 H, =CH). 3-*tert*-Butylpyrrole: NMR δ 1.27 (s, 9 H, $-CH_3$), 6.13 (m, 1 H, =CH), 6.50 (m, 1 H, =CH), 6.61 (m, 1 H, =CH).

Synthesis of 2,5-Dimethylfuran. The furan was prepared from hexane-2,5-dione by the method of Scott and Naples[39] except using Dowex 50W-X8 instead of Amberlyst 15.

Photooxidation of *N*-*tert*-Butylpyrrole in Methanol. In a large water-cooled photocell[11,20] were placed 450 ml of anhydrous methanol, 16 mg of Rose Bengal, and 1.00 g (8.14 mmol) of *N*-*tert*-butylpyrrole. Oxygen was circulated in a closed system. The solution was irradiated using a 500-W Sylvania (N. Q/CL 500) tungsten–halogen quartz lamp operated at 80 V. The progress of the reaction was monitored by measuring the oxygen uptake. The reaction was complete within 22 min, during which ca. 100% equivalent of O_2 ($t_{1/2}$ = 11 min) was consumed. The solvent was removed at 40–50° using a rotary evaporator to yield 1.37 g of crude photoproducts. The crude mixture was partially separated by column chromatography on silica gel (2.3 × 45 cm) using ethyl acetate (500 ml). Further purification by preparative thin layer chromatography on silica gel (ethyl acetate or chloroform) gave the following products.

5-Hydroxy-*N*-*tert*-butyl-Δ^3-pyrrolin-2-one (5): R_f 0.45 (ethyl acetate); 218 mg, 17% isolated yield; mp 75–76°; NMR δ 1.50 (s, 9 H, $-CH_3$), 3.70 (br s, 1 H, –OH), 5.60 (s, 1 H, CH—O), 5.98 (d, 1 H, J = 6 Hz, CHC=O), 6.88 (dd, 1 H, J = 6 and 2 Hz, O=C–CuCH); mass spectrum *m/e* (rel intensity) 155 (M^+, 45), 140 (M – CH_3, 62), 57 (C_4H_9, 100); ir ($CHCl_3$) ν 3350, 1688, 1610 cm^{-1}.

Anal. Calcd for $C_8H_{13}NO_2$: mol wt, 155.09462. Found: 155.09310.

5-Methoxy-*N*-*tert*-butyl-Δ^3-pyrrolin-2-one (4): R_f 0.58 (ethyl acetate); 281 mg, 21% isolated yield; brown oil; NMR δ 1.42 (s, 9 H, $-CH_3$), 3.13 (s, 3 H, OCH_3), 5.58 (s, 1 H, CHO), 6.12 (d, 1 H, J = 6 Hz, CHC=O), 6.79 (dd, 1 H, J = 6 and 2 Hz, O=C–C=CH); mass spectrum *m/e* (rel intensity) 169 (M^+, 6), 153 (M – CH_4, 100), 138 (M – OCH_3, 60%); ir ($CHCl_3$) ν 1690, 1615 cm^{-1}.

Anal. Calcd for $C_9H_{15}NO_2$: mol wt, 169.11027. Found: 169.11051.

***N*-*tert*-Butylmaleimide (6):** R_f 0.63 (chloroform); 60 mg, 5% isolated yield; oil; NMR δ 1.58 (s, 9 H, CH_3), 6.58 (s, 2 H, C=CH); mass spectrum *m/e* (rel intensity) 153 (M^+, 1), 138 (M – CH_3, 100), 57 (C_4H_9, 12); ir ($CHCl_3$) ν 1710 cm^{-1}.

Anal. Calcd for $C_8H_{11}NO_2$: mol wt, 153.0789. Found: 153.0787.

Photooxidation of *N*-*tert*-Butylpyrrole in Acetone. The reaction was carried out essentially as described for *N*-*tert*-butylpyrrole in methanol using 37 mg of Methylene Blue and 1.00 g (8.15 mmol) of *N*-*tert*-butylpyrrole, except that an operating voltage of 100 V was used. After 130 min, 8.15 mmol of O_2 was consumed ($t_{1/2}$ = 47 min). The solvent was removed at 30–40° using a rotary evaporator to yield 1.49 g of crude photoproducts. The crude mixture was partially separated by column chromatography on silica gel (2.3 × 45 cm) using ethyl acetate eluent (300 ml), and further purified by preparative thin layer chromatography silica gel (ether) to give the following photoproducts.

5-Hydroxy-*N*-*tert*-butyl-Δ^3-pyrrolin-2-one (5): R_f 0.38 (ether); 290 mg, 23%, isolated yield; NMR and ir matched those of the authentic sample.

β-(*N*-*tert*-butylformamido)acrolein (14): R_f 0.46 (ether); 160 mg, 13% isolated yield; mp 59–62°; NMR δ 1.57 (s, 9 H, $-CH_3$), 6.50 (dd, 1 H, J = 7 and 4 Hz, CHC=O), 7.39 (d, 1 H, J = 7 Hz, CHN), 8.70 (s, 1 H, NCHO), 9.33 (d, 1 H, J = 4 Hz, CCHO); mass spectrum *m/e* (rel intensity) 155 (M^+, 8), 126 (M – CHO, 62); 98 (M – C_4H_9, 17); ir ($CHCl_3$) ν 1695, 1678, 1618 cm^{-1}.

Anal. Calcd for $C_8H_{13}NO_2$: mol wt, 155.09462. Found: 155.0946.

Photooxidation of 2-*tert*-Butylpyrrole in Methanol. The photooxidation was carried out in the same manner as for *N*-*tert*-butylpyrrole using 1.00 g (8.15 mmol) of 2-*tert*-butylpyrrole and 18 mg of Rose Bengal in 450 of methanol. The reaction was complete within 50 min taking up 10 mmol of oxygen ($t_{1/2}$ = 9 min). Evaporation of the solvent resulted in 1.50 g of crude photoproducts. The crude mixture was partially separated by silica gel column chromatography and further purified by preparative thin layer chromatography on silica gel to give the following photoproducts.

5-Hydroxy-5-*tert*-butyl-Δ^3-pyrrolin-2-one (8): R_f 0.32 [$CHCl_3$–MeOH (9:1)]; 132 mg, 12%; mp 195–197° dec [sublimed at 95° (0.01 Torr)]; NMR (Me_2SO-d_6) δ 0.96 (s, 9 H, $-CH_3$), 5.70 (br s, 1 H, OH), 5.94 (d, 1 H, J = 6 Hz, CHC=O), 7.05 (d, 1 H, J = 6 Hz, CH=C–C=O), 8.14 (br s, 1 H, NH); mass spectrum *m/e* (rel intensity) 155 (M^+, 1), 98 (M – C_4H_9, 84), 57 (C_4H_9, 100); ir (KBr) ν 3210, 1710, 1590 cm^{-1}.

Anal. Calcd for $C_8H_{13}NO_2$: mol wt, 155.09462. Found: 155.0946.

5-Methoxy-5-*tert*-butyl-Δ^3-pyrrolin-2-one (7): R_f 0.58 [$CHCl_3$–MeOH (9:1)]; 557 mg, 23%; mp 126–129° dec [sublimed at 78° (0.02 Torr)]; NMR δ 1.01 (s, 9 H, $-CH_3$), 3.10 (s, 3 H, OCH_3), 6.15 (d, 1 H, J = 6 Hz, CHC=O), 6.80 (d, 1 H, J = 6 Hz, CH=C–C=O), 7.69 (br s, 1 H, NH); mass spectrum *m/e* (rel intensity) 169 (M^+, 1), 112 (M – C_4H_9, 42), 57 (C_4H_9, 100); ir (KBr) ν 3200, 3080, 1688 cm^{-1}.

Anal. Calcd for $C_9H_{15}NO_2$: mol wt, 169.11027. Found: 169.10882.

Pivalamide (9): R_f 0.33 (ethyl acetate); 27 mg, 3%; mp 156–156.5° (lit.[40] mp 155–156°), white leaflet crystal [sublimed at 90° (0.02 Torr)]; NMR δ 1.23 (s, 9 H, $-CH_3$), 5.58 (br s, 2 H, NH); ir ($CHCl_3$) ν 3550, 3430, 1760 cm^{-1}; mass spectrum *m/e* (rel intensity) 101 (M^+, 6), 57 (C_4H_9, 100).

Photooxidation of 2-*tert*-Butylpyrrole in Acetone. The photooxidation was carried out similarly to that of *N*-*tert*-butylpyrrole, using 1.00 g (8.15 mmol) of 2-*tert*-butylpyrrole and 35 mg of Methylene Blue in 450 ml of anhydrous acetone. The reaction was complete within 120 min, taking up 10 mmol of O_2 ($t_{1/2}$ = 38 min). Evaporation of solvent resulted in 1.49 g of crude photoproducts. The crude photoproducts were separated and purified as for *N*-*tert*-butylpyrrole. The following photoproducts were identified.

5-*tert*-Butyl-Δ^4-pyrroline-2,3-dione (15): R_f 0.42 [$CHCl_3$–ether (1:1)]; 101 mg, 8%; orange solid, mp 110–135° [sublimed at 78° (0.03 Torr)]; NMR δ 1.30 (s, 9 H, *t*-Bu), 5.21 (d, 1 H, OHC=C, J = 2 Hz); mass spectrum *m/e* (rel intensity) 153 (M^+, 43), 110 (40), 67 (100), 57 (C_4H_9, 35); ir (KBr) ν 1768, 1750 (sh), 1718, 1695 cm^{-1} (sh).

Anal. Calcd for $C_8H_{11}NO_2$: mol wt, 153.07897. Found: 153.0789.

2-Hydroxy-2-*tert*-Butyl-Δ^4-pyrrolin-3-one (16): R_f 0.68 [$CHCl_3$–MeOH (9:1)]; 15 mg, 1%; mp 157–159° dec; NMR (Me_2SO-d_6) δ 0.82 (s, 9 H, *t*-Bu), 6.05 (d, 1 H, CHC=O, J = 6 Hz), 7.10 (d, 1 H, CH=C–C=O, J = 6 Hz), 8.36 (br s, 1 H, NH); mass spectrum *m/e* (rel intensity) 155 (M^+, 6), 138 (M − OH, 33), 98 (M − C_4H_9, 100), 57 (C_4H_9, 46); ir (KBr) ν 3345, 3090, 3210, 1685 cm^{-1}.

Anal. Calcd for $C_8H_{13}NO_2$: mol wt, 155.09462. Found: 155.0946.

5-Hydroxy-5-*tert*-butyl-Δ^3-pyrrolin-2-one (8): R_f 0.35 [$CHCl_3$–MeOH (9:1)]; 249 mg, 20%; mp 195–197° [sublimed at 95° (1.01 Torr)]; ir and NMR matched those of authentic sample.

Pivalamide (9): R_f 0.33 (ethyl acetate); 39 mg, 5%; mp 156–156.5°; ir and NMR matched those of the authentic sample.

Photooxidation of 3-*tert*-Butylpyrrole in Methanol. The photooxidation was carried out as described for *N*-*tert*-butylpyrrole in methanol using 0.997 g (8.15 mmol) of 3-*tert*-butylpyrrole, 17 mg of Rose Bengal in 450 ml of anhydrous methanol. The reaction was completed within 14 min consuming 9.16 mmol of O_2 ($t_{1/2}$ = 7.5 min). Evaporation of the solvent gave 1.44 g of crude photoproducts. The crude mixture was separated and purified as for *N*-*tert*-butylpyrrole, and the following photoproducts were identified.

5-Hydroxy-3-*tert*-butyl-Δ^3-pyrrolin-2-one (12): R_f 0.59 [$CHCl_3$–MeOH (9.1)]; 136 mg, 11%; oil; NMR δ 1.23 (s, 9 H, $-CH_3$), 4.61 (br s, 1 H, –OH), 5.53 (br s, 1 H, CHO), 6.56 (m, 1 H, CH=C–C=O), 7.52 (br s, 1 H, NH); mass spectrum *m/e* (rel intensity) 154 (M − 1, 3), 83 (100), 85 (65); ir (KBr) ν 3220, 1680 cm^{-1}.

Anal. Calcd for $C_8H_{13}NO_2$: mol wt, 155.09462. Found: 155.0946.

5-Methoxy-3-*tert*-butyl-Δ^3-pyrrolin-2-one (11): R_f 0.59 (ether); 464 mg, 34%; mp 98–99°; NMR δ 1.28 (s, 9 H, $-CH_3$), 3.32 (s, 3 H, OCH_3), 5.32 (m, 1 H, CHO), 6.47 (m, 1 H, CH=C–C=O), 7.46 (br s, 1 H, NH); mass spectrum *m/e* (rel intensity) 169 (M^+, 38), 152 (M − CH_3, 100), 138 (M − OCH_3, 74); ir (KBr) ν 1708, 1675 cm^{-1}.

Anal. Calcd for $C_9H_{15}NO_2$: mol wt, 169.11027. Found: 169.10713.

5-Methoxy-4-*tert*-butyl-Δ^3-pyrrolin-2-one (10): R_f 0.72 [$CHCl_3$–MeOH (9:1)]; 137 mg, 10%; oil; NMR δ 1.24 (s, 9 H, $-CH_3$), 3.35 (s, 3 H, OCH_3), 5.51 (m, 1 H, CHO), 5.89 (m, 1 H, CHC=O), 8.09 (br s, 1 H, NH); mass spectrum *m/e* (rel intensity) 169 (M^+, 1), 137 (M − OCH_3, 77), 112 (M − C_4H_9, 100); ir (KBr) ν 1708 cm^{-1}.

Anal. Calcd for $C_9H_{15}NO_2$: mol wt, 169.11027. Found: 169.10713.

3-*tert*-Butylmaleimide (13). R_f 0.87 (ether); 386 mg, 31%; mp 153–154°; NMR δ 1.32 (s, 9 H, $-CH_3$), 6.22 (m, 1 H, CHC=O); mass spectrum *m/e* (rel intensity) 153 (M^+, 3), 95 (M − C_4H_9, 47), 67 (100); ir (KBr) ν 1765, 1715 cm^{-1}.

Anal. Calcd for $C_8H_{11}NO_2$: mol wt. 153.07897. Found: 153.07873.

Photooxidation of 3-*tert*-Butylpyrrole in Acetone. The photooxidation was carried out similarly to that of *N*-*tert*-butylpyrrole using 1.001 g (8.15 mmol) of 3-*tert*-butylpyrrole and 36 mg of Methylene Blue in 450 ml of anhydrous acetone. The reaction was complete within 100 min consuming 10.9 mmol of oxygen ($t_{1/2}$ = 30 min). Evaporation of solvent resulted in 1.604 g of crude photoproducts. The crude mixture was separated and purified as the same manner as *N*-*tert*-butylpyrrole. The following photoproducts were identified.

5-Hydroxy-3-*tert*-butyl-Δ^3-pyrrolin-2-one (12): R_f 0.29 (ether); 223 mg, 18%; oil; ir, NMR and mass spectrum those of matched authentic sample.

5-Hydroxy-4-*tert*-butyl-Δ^3-pyrrolin-2-one (17): R_f 0.14 (ether); 72 mg, 6%; mp 184.5–185.5° (recrystallized from acetone–chloroform); NMR (acetone-d_6) 1.25 (s, 9 H, $-CH_3$), 5.66 (br, 2 H, CH=C–CO, CHO overlap), 2.87 (br, 1 H, OH), 7.20 (br, 1 H, NH); mass spectrum *m/e* (rel intensity) 155 (M^+, 14), 138 (M − OH, 9), 99 (M − C_4H_8, 100), 57 (C_4H_9, 76); ir (KBr) ν 3250, 1690 cm^{-1}.

Anal. Calcd for $C_8H_{13}NO_2$: mol wt, 155.09462. Found: 155.0944.

3-Hydroxy-3-*tert*-butyl-Δ^4-pyrrolin-2-one (18): R_f 0.40 (ether); 53 mg, 4%; oily solid; NMR δ 1.24 (s, 9 H, *t*-Bu), 5.90 (d, 1 H, CH=CN, J = 2 Hz), 6.33 (d, 1 H, C=CHN, J = 2 Hz); mass spectrum *m/e* (rel intensity) 155 (M^+, 37), 138 (M − OH, 88), 99 (M − C_4H_8, 78), 67 (100), 57 (C_4H_9, 65); ir (KBr) ν 3250, 1700 cm^{-1}.

Anal. Calcd for $C_8H_{13}NO_2$: mol wt, 155.09462. Found: 155.0946.

3-*tert*-Butylmaleimide (13): R_f 0.87 (ether); 593 mg, 43%; mp 153–154°; ir, NMR, and mass spectrum matched those of the authentic sample.

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