isomerization of 1,3-pentadiene[14] indicates an intersystem crossing yield within experimental error of unity. However, singlet **1** apparently is partially quenched by its double bond, since the intercept of a sensitization plot[31] is significantly above unity (1.15).

Finally, these results provide a fairly clear picture of the competing reactions of the excited CT complex. Scheme III is suggested by our measured triplet, oxetane, and isomerization yields and by the observation that the photostationary trans/cis ratio from **1** is characteristic of that from chemical (Schenck) isomerization.[32] The conclusion that half the complex decays to ground state reactant is based on the assumption that reversion of both diradicals to ground state would yield geometric isomerization of the double bond. As usual in triplet state photochemistry, product quantum yields reveal very little about excited state rate constants when one or more metastable photoproducts can revert to ground state reactant.

Acknowledgment. We gratefully note partial support of this work by separate National Science Foundation grants to both laboratories.

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(10) Details of their preparation will be presented in the full paper.

(11) Since the products do not possess unexpected structures, details of their characterization will be delayed to our full papers.

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Received September 9, 1975

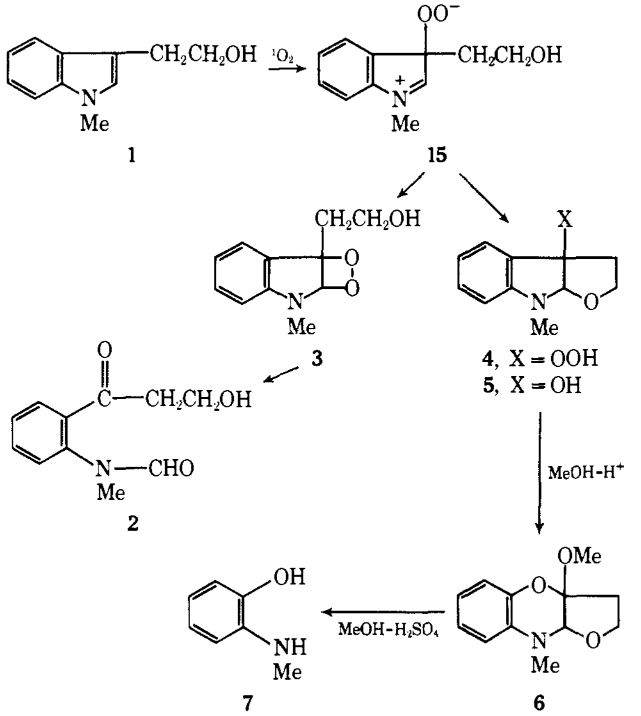
Indole–Singlet Oxygen Reactions. A Novel Rearrangement of the Peroxidic Intermediates to 2,3-Dihydro-1,4-benzoxazines[1]

Sir:

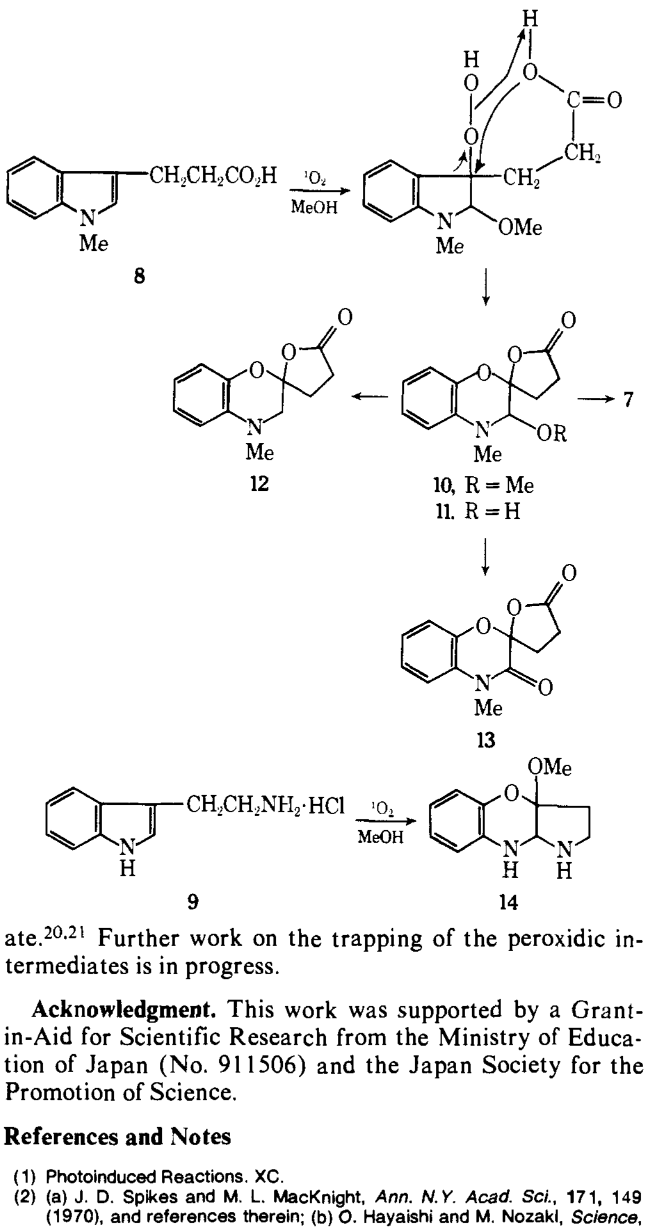
Although extensive studies of the reaction of indoles, including tryptophan,[2] with molecular oxygen have been made,[2,3] there are very few reports on the nature of the peroxidic intermediates involved in the reactions, with the exception of 3-hydroperoxyindolenines.[2g,3] We report here results of the reaction of 3-substituted indoles with singlet oxygen, in which we show that (i) the peroxidic intermediates are efficiently intercepted by the functional groups of the side chain to yield 3-hydroperoxyindolines, and that (ii) the hydroperoxidic products readily undergo a new type of rearrangement to give 2,3-dihydro-1,4-benzoxazines in the presence of catalytic amounts of acid. Thus the results provide a new method for the oxidative transformation of indoles into 1,4-benzoxazine systems.

Rose bengal-sensitized photooxygenation[4] of *N*-methyltryptophol (**1**) (2 m*M*) in methanol at room temperature gave a normal C_2-C_3 ring cleavage product, **2**[5] (90%), which is generally considered to be formed through dioxetane **3**.[6,7] However, when the same photooxygenation of **1** (2 m*M*) was carried out at −70° until 1 molar equiv of oxygen was absorbed and the reaction mixture was stripped of solvents under vacuum at 0°, 3-hydroperoxyindoline (**4**) was obtained in 95% yield; dioxetane **3** was not detected.[8] The structure of **4** was assigned on the basis of the following spectral data and chemical reactions: uv (EtOH) 249 (log ϵ 3.84), 298 nm (log ϵ 3.20); ir (Nujol) 3400 cm^{-1}; NMR ($CDCl_3$) δ 2.12–2.43 (m, 2 H, CH_2), 2.87 (s, 3 H, NMe), 3.30–4.12 (m, 2 H, CH_2O), 5.13 (s, 1 H, NCHO), 5.47 (s, 1 H, OOH, exchangeable), 6.33–7.29 (m, 4 H, aromatic H); mass spectrum (*m/e*, 70 eV) 207 (M^+, 5%), 191 ($M^+ - O$, 6%), 189 ($M^+ - H_2O$, 9%), 174 ($M^+ -$ OOH, 6%), 173 ($M^+ - H_2O_2$, 10%), 142 (100%). Dimethyl sulfide reduction of **4** in methanol gave **5**[5] (90%) (mp 63–64°; uv (EtOH) 249 (log ϵ 3.82), 306 nm (log ϵ 3.16); ir (Nujol) 3290 cm^{-1}; NMR ($CDCl_3$) δ 2.20 (s, 1 H, OH), 2.25–2.50 (m, 2 H, CH_2), 2.90 (s, 3 H, NMe), 3.38–4.13 (m, 2 H, CH_2O), 5.15 (s, 1 H, NCHO), 6.35–7.33 (m, 4 H, aromatic H); mass spectrum (*m/e*) 191 (M^+)) which was identical with the sample prepared by the oxidation of **1** with *m*-chloroperbenzoic acid in methylene chloride (48%). Treatment of the hydroperoxide **4** with methanol containing catalytic amounts of HCl at room temperature gave 2,3-dihydro-1,4-benzoxazine (**6**)[5,9] (75%): a pale yellow oil, bp 64–65° (1 mmHg); uv (EtOH) 243 (log ϵ 3.77), 288 nm (log ϵ 3.23); ir (Nujol) 1120, 1050 cm^{-1}; NMR ($CDCl_3$) δ 2.20–

Scheme I



Scheme II



2.50 (m, 2 H, CH_2), 3.07 (s, 3 H, NMe), 3.43 (s, 3 H, OMe), 3.90-4.17 (m, 2 H, OCH_2), 4.85 (s, 1 H, NCHO), 6.67-6.93 (m, 4 H, aromatic H); mass spectrum (*m/e*) 221 (M^+). Heating of **6** in methanol and 2 *N* H_2SO_4 (2:1) at reflux produced **7** (48%) (Scheme I).

Similar rearrangement was observed in the photooxygenation of *N*-methylindole-3-propionic acid (**8**) and tryptamine (**9**). In the case of **8**, the addition of HCl is not necessary for the rearrangement. Photooxygenation of **8** (10 m*M*) in methanol at room temperature led to the clean formation of **10**[5] (95%): mp 114-115°; uv (MeOH) 240 (log ϵ 4.01), 287 nm (log ϵ 3.54); ir (Nujol) 1780 cm^{-1}; NMR ($CDCl_3$) δ 2.37-2.83 (m, 4 H, CH_2CH_2), 3.30 (s, 3 H, NMe), 3.40 (s, 3 H, OMe), 4.53 (s, 1 H, NCHO), 6.70-6.90 (m, 4 H, aromatic H); mass spectrum (*m/e*) 249 (M^+). Treatment of **10** with aqueous acetone gave **11**[5,10] (98%), which on catalytic hydrogenation (PtO_2) yielded **12**[5,11] (35%). Oxidation with chromic acid in a two-phase system gave the corresponding amide **13**[5,12] (52%). As in the case of **6**, heating of **10** in methanolic H_2SO_4 gave **7** (37%). Similarly, methylene blue-sensitized photooxygenation of tryptamine hydrochloride **9** in methanol at room temperature yielded the corresponding 2,3-dihydro-1,4-benzoxazine (**14**)[5] (89%): a colorless oil, bp 159-160° (1 mmHg); uv (EtOH) 242 (log ϵ 3.51), 289 nm (log ϵ 3.29); ir (neat) 3320, 2960, 1110, 1040 cm^{-1}; NMR ($CDCl_3$) δ 1.90-2.33 (m, 2 H, CH_2), 2.48 (s, 1 H, NH), 2.57 (s, 1 H, NH), 2.93-3.31 (m, 2 H, NCH_2), 3.40 (s, 3 H, OMe), 4.33 (s, 1 H, NCHN), 6.49-7.00 (m, 4 H, aromatic H); mass spectrum (*m/e*) 206 (M^+) (Scheme II). These photooxygenations were inhibited by the addition of known singlet oxygen quenchers, 1,4-diazabicyclo[2.2.0]octane[13] or triethylamine,[14] indicating that the reactions are singlet oxygen-mediated reactions.[15]

The present results provide a simple and general method for the transformation of indoles into 2,3-dihydro-1,4-benzoxazines.[16] The results also offer a suggestive information that such transformations may potentially be involved in the oxidation of indoles in biological systems.[18] It is not known whether the hydroperoxyindoline **4** is formed from a zwitterionic peroxide **15**[6,19] or from a perepoxide intermediate.[20,21] Further work on the trapping of the peroxidic intermediates is in progress.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan (No. 911506) and the Japan Society for the Promotion of Science.

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(10) Mp 118–120°; uv (EtOH) 244 (log ϵ 4.02), 290 nm (log ϵ 3.58); ir (Nujol) 3300, 1780 cm^{-1}; NMR (DMSO-d_6) δ 2.37–2.83 (m, 4 H), 3.07 (s, 3 H), 4.77 (d, 1 H, J = 8.0 Hz), 6.30 (d, 1 H, J = 8.0 Hz), 6.70–6.90 (m, 4 H); mass spectrum (*m/e*) 235 (M^+).
(11) Mp 69–71°; uv (EtOH), 252 (log ϵ 3.47), 295 nm (log ϵ 3.08); ir (Nujol) 1780 cm^{-1}; NMR ($CDCl_3$) δ 2.20–2.87 (m, 4 H), 2.97 (s, 3 H), 3.39 (s, 2 H), 6.70–6.90 (m, 4 H); mass spectrum (*m/e*) 219 (M^+).
(12) Mp 124–125°; uv (EtOH), 250 (log ϵ 3.58), 278 (log ϵ 3.34), 285 nm (log ϵ 3.31); ir (Nujol) 1785, 1685 cm^{-1}; NMR ($CDCl_3$) δ 2.30–3.00 (m, 4 H), 3.43 (s, 3 H), 7.00–7.20 (m, 4 H); mass spectrum (*m/e*) 233 (M^+).
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(21) It seems unlikely that **4** is formed from the dioxetane **3**, since dioxetanes so far obtained are not known to undergo such a nucleophillic displacement reaction by alcohols.[7b,22] According to the MINDO/3 calculations, the reactions of singlet oxygen with enamines have been predicted to take place in steps via zwitterionic intermediates.[23]
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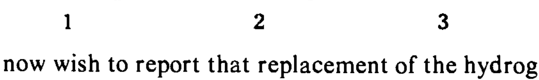
Received July 21, 1975

Effect of Stabilizing Groups on the Extent of Long Range π Electron Participation in Carbanions

Sir:

It has been recently reported by Brown and Occolowitz[1] that bicyclooctadiene (**1**) undergoes base-catalyzed hydrogen-deuterium exchange at C_4 $10^{4.5}$ times faster than its saturated analogue, monoene **2**. The increased reactivity of **1** was attributed to the greater stability of its incipient carbanion intermediate during deuterium exchange, in which the negative charge could interact not only with the carbon-carbon double bond at $C_{2,3}$ but also with the $C_{6,7}$ double bond, thereby producing a bishomoaromatic cyclopentadienyl species as represented by structure **3**. The participation of the $C_{6,7}$ double bond in delocalizing the negative charge was subsequently confirmed by Winstein and his co-workers[2] who were able to generate anion **3** in sufficiently large quantities to study its ^1H NMR spectrum. The latter clearly supported the delocalized nature of the anion.

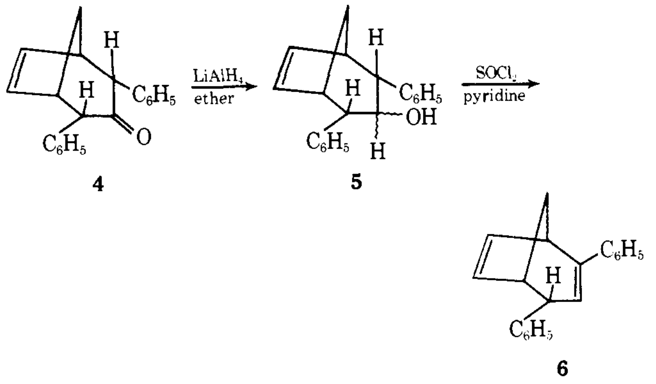


1 2 3

We now wish to report that replacement of the hydrogens at C_2 and C_4 in bicyclic diene **1** by phenyl groups results in totally eliminating the charge delocalization from C_4 to the carbon-carbon double bond at $C_{6,7}$. This conclusion was reached on the basis of the fact that 2,4-diphenylbicyclo[3.2.1]octa-2,6-diene (**6**) and its saturated analogue **9** were found to undergo base-catalyzed hydrogen-deuterium exchange at C_4 at essentially the same rate (Table I).

A number of reports have appeared in the recent literature indicating that the extent of neighboring group participation in stabilizing an incipient carbonium ion is inversely proportional to the stability rendered to the developing charge by groups directly attached to the cationic center.[3,4] In turn, this principle has been extensively used as a very effective tool in determining the extent of π and σ participation in a large variety of carbonium ions.[4,5] The present report constitutes the first study demonstrating that the above principle is equally applicable to carbanions stabilized by π electron participation.

Scheme I



2,4-Diphenylbicyclo[3.2.1]octa-2,6-diene (**6**) was synthesized as outlined in Scheme I. Thus, treatment of *cis-endo*-diphenyloctenone[6] (**4**) (40 mmol) in ether with 66 mmol of $LiAlH_4$ at reflux for 48 hr, followed by the usual work-up, afforded 8.0 g (73%) of alcohol[7] **5**: mp 78-83° from 95% ethanol; ir 3570 cm^{-1} (OH); ^1H NMR (DMSO-d_6) δ 2.12 (m, 2 H, H_8), 2.80 (m, 2 H, $H_{1,5}$), 3.05 (s, 1 H, OH), 3.32 (m, 2 H, $H_{2,4}$), 4.22 (m, 1 H, H_3), 6.49 (s, 2 H, $H_{6,7}$), 7.27 (m, 10 H, aromatic protons); mass spectrum[8] (relative intensities) 276 (M^+, 12%), 258 (19%), 157 (53%), 120 (30%), 91 (100%).

Alcohol **5** (29.7 mmol) was subsequently treated with purified thionyl chloride (44.6 mmol) in dry pyridine at room temperature for 6 hr to produce, after work-up and purification, 6.2 g (80%) of 2,4-diphenylbicyclo[3.2.1]octa-2,6-diene[7] (**6**): mp 43-45° from methanol; ^1H NMR[9] ($CDCl_3$) δ 2.27 (m, 2 H, H_8), 3.05 (m, 1 H, H_5), 3.25 (m, 1 H, H_1), 3.82 (m, 1 H, H_4), 5.32 (doublet of doublets, 1 H, H_6), 5.72 (m, 1 H, H_3), 6.47 (doublet of doublets, 1 H, H_7), 7.31 (m, 10 H, aromatic); mass spectrum[8] (relative intensities) 258 (M^+, 71%), 230 (40%), 154 (40%), 105 (100%), 91 (82%).

2,4-Diphenylbicyclo[3.2.1]oct-2-ene (**9**) was synthesized as shown in Scheme II. Thus, bicyclooctenone (**4**) (38.3 mmol) was treated with *p*-toluenesulfonylhydrazine (56.4 mmol) and a catalytic amount of hydrochloric acid in methanol at reflux for 23 hr to afford, after work-up and purification, 8.3 g (78%) of diphenyloctanone[7,10] **7**: mp 114-116° from methanol; ir 1700 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.02 (m, 6 H, H_8 and $H_{6,7}$), 2.78 (m, 2 H, $H_{1,5}$), 3.93 (d, 2

Scheme II