which time the absence of Zeise's dimer was confirmed by ^{1}H NMR spectroscopy. The time needed for reaction varied with the amount of Zeises' dimer used; thus in reaction with $[Pt_2Cl_4(C_2H_4)_2]$ (0.2 g) and *trans*-1,2-diphenylcyclopropane (0.4 g) in ether (15 cm^3) the reaction was complete in 24 h. The insoluble product was filtered off, washed with ether, and dried under vacuum; yield 86%, Anal. for C, H.

Similarly, crude dichloro(*cis*-diphenylpropane-1,3-diyl)platinum(IV) was prepared from $[Pt_2Cl_4(C_2H_4)_2]$ (0.3 g) and *cis*-1,2-diphenylcyclopropane (0.5 g) in refluxing ether (20 cm^3) for 7 days.

Dichlorobis(pyridine)(*trans*-diphenylpropane-1,3-diyl)platinum(IV). Dichloro(*trans*-diphenylpropane-1,3-diyl)platinum(IV) (0.15 g) suspended in CH_2Cl_2 (5 cm^3) was treated with pyridine (ca. 0.2 g) until a clear solution was obtained. The solvent was evaporated, and the *product* was washed with pentane and dried under vacuum: yield 67%, mp 108 °C dec, Anal. for C, H, N.

Dichlorobis(4-*tert*-butylpyridine)(*trans*-diphenylpropane-1,3-diyl)platinum(IV). This was prepared in a similar way but was purified by chromatography through silica gel, eluting with CH_2Cl_2: yield 86%, Anal. for C, H, N.

Dichlorobis(4-*tert*-butylpyridine)(*trans*-1,3-di-4-tolylpropane-1,3-diyl)platinum(IV). A suspension of $[Pt_2Cl_4(C_2H_4)_2]$ (0.8 g) in anhydrous ether (30 cm^3) was heated under reflux for 3 days with *trans*-1,2-di-4-tolylcyclopropane (0.8 g). The precipitate was filtered off and suspended in CH_2Cl_2 (10 cm^3) and 4-*tert*-butylpyridine was added dropwise with stirring until a clear solution was obtained. The solvent was evaporated under vacuum, and the crude product was purified by column chromatography through silica gel, eluting with CH_2Cl_2, and was isolated as a pale yellow solid: yield 0.82 g (80%), mp 290 °C dec, Anal. for C, H, N.

Reactions with Cyanide and Triphenylphosphine. A solution of dichlorobis(pyridine)(*trans*-diphenylpropane-1,3-diyl)platinum(IV) (25 mg) in $CHCl_3$ (3 cm^3) was heated at 45 °C for 2 days. The product was isolated and redissolved in $CHCl_3$ and then an aqueous solution of potassium cyanide (3 cm^3, 0.05 M) was added. The mixture was shaken for several minutes, then the organic layer was separated, dried with $MgSO_4$, and filtered. Analysis of the filtrate by GLC showed the presence of *trans*- and *cis*-1,2-diphenylcyclopropane in relative amounts 86% and 14%, respectively.

In reactions with triphenylphosphine, the phosphine (2 mol) was added to the platinacyclobutane (1 mol) in $CHCl_3$. The precipitate of $[PtCl_2(PPh_3)_2]$ was removed by filtration, and the filtrate was analyzed as above.

1-Phenyl-2-deuteriocyclopropane was analyzed, after displacement from the platinum complexes by triphenylphosphine, by NMR spectroscopy. The methylene groups of the cyclopropane give signals at 0.64 ppm (H atoms cis to Ph) and at 0.88 ppm (H atoms trans to Ph). In our best sample of the parent cyclopropane this ratio is 1.75:1 from which the ratio *trans*-:*cis*-1-phenyl-2-deuteriocyclopropane = 91:9. The same ratio was found in the cyclopropane formed from the initially formed and the isomerized platinacyclobutanes. Similarly, a sample containing 80% trans and 20% cis isomer gave the identical mixture on reaction of isomerized platinacyclobutane with PPh_3.

Acknowledgment. We thank SRC (UK) and NSERC (Canada) for financial support, NATO for a travel grant, and Johnson-Matthey Ltd. for the generous loan of platinum compounds. Acknowledge is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Response of *syn*-1,2,3,4,5,6,7,8-Octahydro-1,4:5,8-dimethanonaphthalene and Related Molecules to Oxidation with Ozone, Singlet Oxygen, and Triplet Oxygen. Strain and Steric Effects as Controllers of Reactivity

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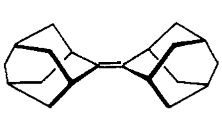
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received April 25, 1980*

Abstract: The title compound (**4**), its 2,3-benzo derivative (**5**), and dimethyl *syn*-1,4,5,8-tetrahydro-1,4:5,8-dimethanonaphthalenedicarboxylate (**6**) have been synthesized and their reactivity toward various oxygenating agents evaluated. Whereas **4** is unreactive toward triplet oxygen, **5** experiences 80% conversion to exo epoxide **19** (55%) and diketone **20** (45%) during 28 h in benzene solution at 10 °C. By way of comparison, diester **6** is exceptionally reactive in air, giving chiefly epoxide **21**. The stereochemistry of **21** was suggested by ^{13}C NMR spectroscopy and substantiated by photocyclization to cage diester **22**. In the presence of ozone, **4** is transformed almost completely to diperoxy diketone **25** without regard for solvent polarity (pentane or ethyl acetate). When the ozonolysis is conducted in the presence of TCNE, diketone **26** is formed uniquely. To further test the ability of **4** to undergo 1,3-dipolar cycloaddition, we treated the olefin with phenyl azide. Triazoline **27** was produced; irradiation of this adduct gave aziridine **28**. Under conditions of photooxygenation with methylene blue and tetraphenylporphin as sensitizer, **4** is slowly converted to diketone **26**. With polymer-bound rose bengal as the sensitizer, photoepoxidation also is observed. Conclusions dealing with the mechanistic aspects of these reactions are presented and references are made to the possible usefulness of these uniquely structured molecules in the elucidation of transition-state geometries.

A few uniquely constructed olefinic compounds are now known in which attack by a given reagent is severely restricted to approach along a very limited number of geometric planes. As a result, usually preferred modes of reaction may be rendered inoperative and important mechanistic information may consequently be made evident. For example, the special structural features of biadamantylidene (**1**)^1 and 7,7′-binorbornylidene (**2**)^2 provide π-bond faces which are most open and accessible if perpendicular ($\pi^2s + \pi^2a$) attack takes place.^{3} In dehydrojanusene (**3**),^{4} the presence



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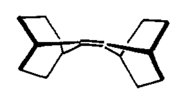

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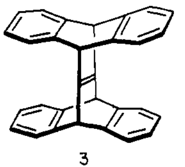

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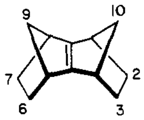
(3) Additional examples include fenchylidene-fenchane, camphenylidene-camphenilane, and camphenylidene-adamantane: McCapra, F.; Beheshti, I. *J. Chem. Soc., Chem. Commun.* **1977**, 517.

of the four benzene rings forces an electrophile of the X = Y type to approach in a plane parallel to the two olefinic carbons, thus nesessitating ($\pi^2s + \pi^2s$) bonding. The special steric hindrance which exists in **3** becomes still more accentuated in *syn*-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanonaphthalene (**4**) where the exo surface of the shared norbornene double bond is blocked by the syn-oriented methano bridge protons.[5] Molecular models clearly show that ($\pi^2s + \pi^2a$) attack is substantively inhibited by the geometric features of the structure. After completion of our work concerning various oxidation reactions of **4** and, to a lesser extent, its more unsaturated congeners **5** and **6**, a report by Bartlett and his co-workers which describes photooxygenation studies on *anti*-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanonaphthalene (**7**) made its appearance.[6] The observations reported herein extend and complement the recently recorded behavior of this somewhat less sterically congested isomer.



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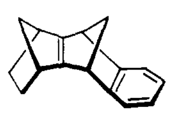

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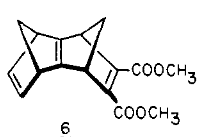

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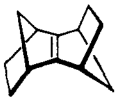

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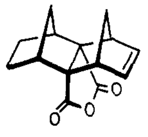


8

Results

Isomerically pure hydrocarbon **4** was readily obtained as before[5a] by stereospecific (endo) cycloaddition of phenyl vinyl sulfone[7] to isodicyclopentadiene followed by reductive desulfonylation.[8] Treatment of the same diene with benzyne provided **5**.[5] The exclusive formation of **6** was realized by means of Diels–Alder reaction of tricyclo[5.2.1.$0^{2,6}$]deca-2,5,8-triene with dimethyl acetylenedicarboxylate.

Although a direct X-ray crystal structure analysis of **4** is presently unavailable, some idea of the steric congestion surrounding the exo and endo faces of its π bond can be derived from the experimentally determined three-dimensional coordinates of the norbornene ring in **8**.[6] From these data, it has been calculated that endo-H_9 lies only 3.416 Å away from endo-H_{10} and coplanar to it, while the endo-H_3/endo-H_6 and endo-H_2/endo-H_7 pairs are but 2.728 Å apart. Figure 1 shows a frontal perspective of the *xz* plane in **4**, a view which clearly shows the relationships of these key hydrogen atoms to the central bond. When the normal van der Waals radii of the obstructing hydrogens (1.2 Å) are taken into account (indicated by circles), the apertures above and below the olefinic center are reduced to 1.016 and 0.328 Å, respectively. In view of the present approximations, it remains possible that the obviously high endo congestion is in actuality somewhat relieved by slight mutual compression of C_9 and C_{10}. Nonetheless, the model suggests not only that electrophiles should exhibit a strong preference for exo approach to **4** but also that the conversion from trigonal to tetrahedral hybridization at C_{4a} and C_{8a} should serve to further reduce the distance separating the ethano bridges.

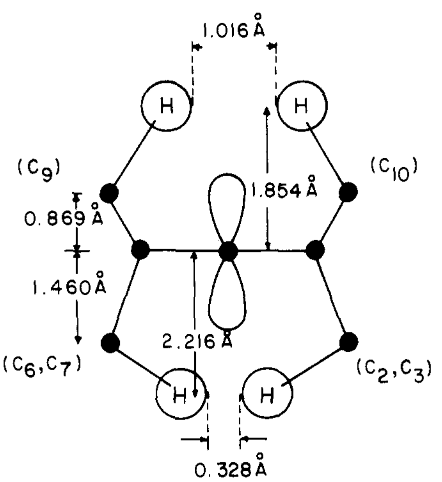
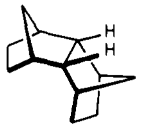


Figure 1. View along the C=C bond of **4**. The circles represent the 1.2-Å van der Waals radius of the blockading hydrogen atoms.

Certain pieces of evidence supportive of these conclusions were available prior to this study. For example, whereas attempts to effect the catalytic hydrogenation of **4** were without success, conversion to **9** (prepared independently by saturation of the well-known 2,6-diene[9]) occurred rapidly in the presence of diimide.[5a] Exo protonation to give **10** was observed upon addition of CD_2Cl_2 solutions of **4** to SO_2ClF-FSO_3H (3:1) at −110 °C. Subsequent quenching of the cation solution with K_2CO_3 in cold methanol gave **11a** and **4**.[10] Epoxidation of **4** with *m*-chloroperbenzoic acid delivered exo epoxide **12** in a reaction which is complete within 10 min at −20 °C. This rate would appear to compare closely to that reported for **2** but be much faster than the qualitative data provided for **1** (6 °C, 24 h) and **3** (room temperature, 1 week). The bromination of **4** similarly proceeds without skeletal rearrangement to give **13**. The extreme steric compression in **11b** is revealed by its rate of solvolysis (3 500 000 times faster than *tert*-butyl *p*-nitrobenzoate), which qualifies this compound as the most highly reactive saturated tertiary derivative presently known.[10]



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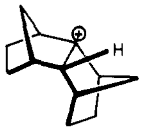

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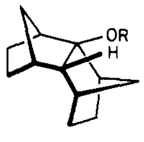
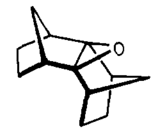


11a, R = CH_3
b, R = PNB



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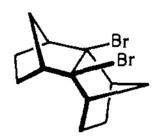

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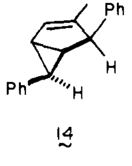
Triplet Oxygen. Preparatively useful reactions of ground-state molecular oxygen, although uncommon, are not unknown. Padwa has recently described the thermal epoxidation of **14** with molecular oxygen (xylene, reflux 48 h, 76%),[11] while Hart has



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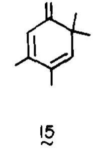

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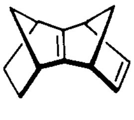
demonstrated that conjugated dienones typified by **15** experience γ,δ-epoxidation when heated in an inert solvent (xylene, reflux 24 h, 51%).[12] 2-Phenylnorbornene is recognized to be subject to similar autoxidation.[13] The $^3O_2$-induced cleavages of tri-*tert*-butylcyclobutadiene[14] and tetrakis(dialkylamino)ethylenes[15] have also been reported. The mechanisms of these reactions remain unclarified. Nonetheless, the extent to which reaction with triplet oxygen might occur was considered by us to be intimately linked to the latent energy of a given molecule.

The significant increase in strain which materializes upon the introduction of one or two added double bonds in **4** was made evident in several ways. By means of photoelectron spectroscopy (courtesy of Professor R. Gleiter), the first π-olefinic ionization potentials of **4** and **5** were determined to be 8.27 and 7.86 eV, respectively. The ^{13}C chemical shift of the trigonal carbons in **4** appears at 151.6 ppm, appreciably upfield of those found in **5** (158.7 ppm) and **16** (157.7 ppm). Intriguingly, the internal sp^2-hybridized carbons of diester **6** exhibit the most pronounced downfield shift yet known for a trigonal center in an isolated double bond (166.0 ppm). Bicyclohexene **17** was the prior record holder (163.5 ppm).[16]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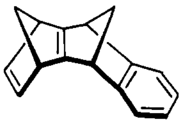
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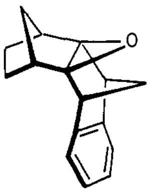
The varied energetic situation in this series reveals itself in chemical reactivity, as expected. We had previously noted that, whereas **5** could be readily obtained from the condensation of benzyne with isodicyclopentadiene, its more unsaturated counterpart **18** could not be isolated, irrespective of stoichiometry. (2 + 2) cycloaddition of a second molecule of benzyne to the central double bond occurs exceedingly rapidly.[5]

To provide an additional basis of comparison, we conducted initially a competition experiment in which equimolar amounts of **4** and **5** were allowed to vie for a limiting quantity of *m*-chloroperbenzoic acid in dichloromethane solution at −20 °C. Under these conditions, **5** was selectively consumed to provide epoxide **19**.



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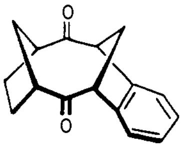


20

When oxygen was bubbled through a cold (10 °C) benzene solution of **5** for 28 h, there was realized an 80% conversion to a mixture of epoxide **19** (55%) and diketone **20** (45%). Additional experiments for varying lengths of time and at different substrate concentrations (see Table I) showed the ratio of **19** and **20** to vary significantly, however. The symmetry of the latter crystalline solid, which exhibited a carbonyl stretching frequency of 1682 cm^{-1}, was apparent from its 9-line ^{13}C NMR spectrum. The exo stereochemical assignment to **19**, like that to **12**, is based in part upon the long-range ^{13}C shielding effects experienced at the methano bridge carbons (C_9, C_{10}). It is now well established where epoxynorbornanes are concerned that the methano bridge carbon in the exo isomer exhibits a chemical shift more than 20 ppm upfield of its counterpart in the endo isomer.[17-19] The effect is clear if comparison is made of the C_7 shifts in norbornane (39.2 ppm) and the *exo*- (26.3 ppm) and *endo*-norbornene oxides (50.6 ppm). In similar fashion, C_9 and C_{10} in **12** (38.9 ppm) appear at a higher field than their counterparts in **9** (47.1 ppm). Because the two methano carbons in **19** exist in quite different environments, the nonbenzo-fused norbornyl bridge carbon (38.8 ppm) is the more useful as a point of reference (vs. 46.9 ppm in dihydro-**5**).

Table I. Molecular Oxygenation of 5 in Benzene[a]

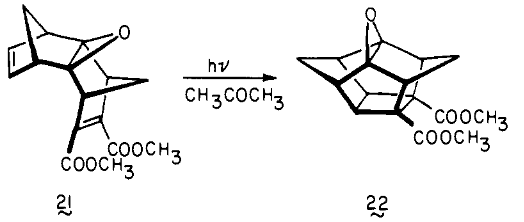
concn, M	time, h	rel % of 19	rel % of 20	% completn
7	14	74	26	41
1.53	48	68	32	81
0.98	48	65	35	55
1.06 × 10^{-2}	48	61	39	23
	65	60	40	31

[a] Product analysis was accomplished by concentrating the reaction mixture and recording the ^{1}H NMR spectrum. The relative percentages of 5, 19, and 20 were determined by machine integration of their respective benzylic bridgehead protons at δ 3.65, 3.40, and 4.23. In each instance, the ^{13}C NMR spectrum was also recorded to confirm the formation of 19 and 20 and the absence of other possible oxidation products.

Evidence for the free-radical nature of the preceding oxidation was provided by adding 2,6-di-*tert*-butyl-*p*-cresol (0.2 equiv) to the reaction mixture. Over the identical period of time originally required to achieve 80% consumption of **5**, the hydrocarbon remained unchanged. At much longer reaction times, the inhibitor itself underwent chemical modification, at which point the previously encountered oxygenation process was seen to resume. Variation of the concentration levels of **5** from 1.1 M to 1.06 × 10^{-2} M had the effect of enhancing somewhat the relative amount of diketone produced (Table I).

Comparable treatment of **4** led to no reaction. Concomitant irradiation from a Sylvania 500-W tungsten halogen lamp (for 3 days) proved equally unadvantageous. Thus, **4** like **1** and **2** is unresponsive to autoxidation.

In striking contrast, diester **6** is so highly reactive toward molecular oxygen that standard combustion analysis of its elemental composition is precluded. When oxygen was bubbled through dichloromethane solutions of **6** at room temperature, reaction was complete in 30 min to give a mixture of products from which **21** was isolated in 59% yield. The ^{13}C NMR spectra of **6** and **21** exhibit signals for the methano carbons at 68.9, 65.8 and 52.4, 52.0 ppm, respectively, as expected for exo orientation of the epoxide oxygen atom in **21**. Since this oxide is easily converted to cage photoproduct **22** by 3500-Å irradiation in acetone or acetonitrile solution, its two isolated π bonds are required to be proximate as shown (eq 1). The ^{13}C NMR spectrum of **22** shows the nine absorptions expected of its C_s symmetry.



21 22 (1)

Ozonolysis. Notwithstanding the long history of ozonolysis and the large surge of interest in this reaction in recent years, a

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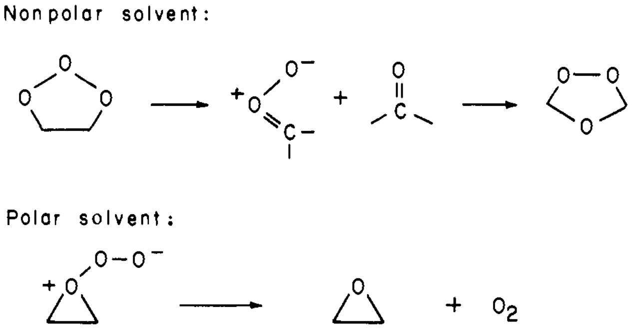
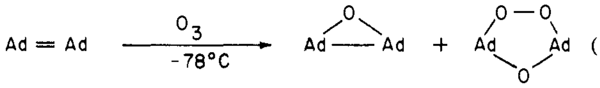
Scheme I



comprehensive mechanistic scheme has remained elusive.[20,21] The entire issue has been further compounded by newly advanced theoretical conclusions.[22-24] The stringent constraints placed upon the process by such sterically congested molecules as **1** and **2** are of considerable interest. To illustrate, **2** reacts with ozone at −78 °C to deliver only the epoxide.[2] In Keul's program to characterize the behavior of biadamantylidene (**1**) toward ozone in nonparticipating solvents,[25] variations in product distribution were seen. While **1** was converted only to epoxide **23** in ethyl acetate solution at −78 °C, the use of pentane under otherwise identical conditions allowed the isolation of ozonide **24** as well (eq 2). Admixture of this pair of solvents in a 1:1 ratio with tetracyanomethylene added led to a comparable distribution of **23** and **24** (no TCNE oxide was isolated).



(2)

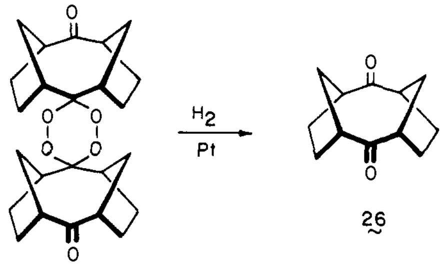
1 **23** **24**

	23	24
pentane	60%	33%
ethyl acetate	92%	0%
pentane–EtOAc (1:1) with TCNE	66%	28%

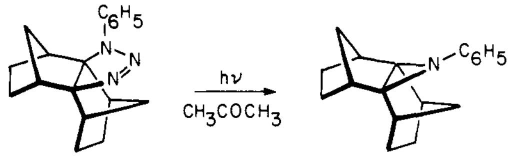
These observations have been rationalized in terms of two competing mechanistic pathways. In the first which is presumably favored in nonpolar media, initial 1,2,3-trioxalane production is followed by fragmentation to a carbonyl oxide–ketone pair which recombines to give isolable ozonide. An increase in solvent polarity was construed as favoring peroxy epoxide production, which intermediate subsequently suffers loss of molecular oxygen to give neutral epoxide (Scheme I).

In the case of **4**, we have observed no solvent effect of a similar nature. In either pentane or ethyl acetate at −78 °C, **4** was converted into a white powdery solid (85%) identified as the diperoxy diketone **25** and to a small amount of a trimeric species. When the ozonolysis was conducted in the presence of TCNE, only diketone **26** (81%) and tetracyanoethylene oxide were obtained (eq 3).

Since mechanistic considerations (see Discussion) dictate that the ability of **4** to enter into 1,3-dipolar cycloaddition reactions be ascertained, an example was studied where the initial adduct was expected to be stable and subject to full characterization. When a solution of **4** and phenyl azide in ethyl acetate was allowed to stand for 4 h at room temperature, the triazoline adduct **27** was produced in 85% yield. The stereochemistry of **27**, initially assigned to conform with earlier findings, was substantiated by photochemical conversion to aziridine **28** (eq 4). The 7-line ^{13}C NMR spectrum of this heterocycle conforms to its C_{2v} symmetry. Equally significant is the upfield chemical shift of its methano bridge carbons (41.9 ppm) which reveals the shielding expected from the syn-disposed nitrogen atom.



25 **26** (3)



27 **28** (4)

Photooxygenation. The behavior of hindered olefins **1** and **2** toward singlet oxygen is unusual in that an epoxide and stable dioxetane can be isolated in both instances. Interestingly, the ratios of these products are highly solvent dependent and affected further by the nature and concentration of sensitizer, intensity and type of light source, and the presence of certain additives.[1,2] Under comparable conditions, fenchylidene–fenchane and camphanylidene–camphenilane give rise to 1,2-dioxalanes of rearranged skeleton, the observations prompting the suggestion that dipolar perepoxide intermediates intervene.[3] Dehydrojanusene (**3**) and *anti*-sesquinorbornene (**7**) have been reported to be unreactive to singlet oxygen when customary reaction conditions are employed. However, both olefins are slowly converted in part to their epoxides (3.8 and 25–40%, respectively) when the photooxygenation is conducted by using irradiation from a 450-W Hanovia mercury arc on dichloromethane or chloroform solutions containing tetraphenylporphin as sensitizer.[4b,6] With biacetyl or benzil as sensitizer and benzene as solvent, **3** and **7** were more rapidly and efficiently converted to their respective epoxides. The absence of dioxetanes and the other unusual features of these reactions were construed to be indications that **3** and **7** do not react directly with singlet oxygen but rather with intermediates produced from certain photosensitizers when chemically activated in this fashion.

Due to the sensitivity of **5** to triplet oxygen, its reactivity under photooxygenation conditions was not examined. However, the photooxygenation of **4** in benzene solution using Photox (polymer-bound rose bengal) as the sensitizer proved to be very sluggish in comparison to **1** and **3**, despite the low ionization potential of **4**. After 80 h, analysis of the reaction mixture by ^{13}C NMR spectroscopy indicated approximately 80% consumption of starting material and formation of epoxide **12** and diketone **26** in a 1:3 ratio. With 2,6-di-*tert*-butyl-*p*-cresol as additive, the identical results were observed; the cresol was also consumed. When methylene blue and tetraphenylporphin were utilized as the sensitizer (benzene solution), diketone production was uniquely observed. Attempts to suppress epoxide formation in other ways (methylene blue in acetone; rose bengal in pyridine) proved abortive, as the oxygenation reaction under these conditions was apparently still slower. The assumed dioxetane precursor of **26** (see Discussion) was not directly observed.

At this point, we recall that Jefford and Boschung also previously observed a dependence between epoxide yield and the particular photosensitizer employed.[26] In a similar vein, Shimizu and Bartlett demonstrated that photooxidation of various selected olefins in benzene solution by using the n → π^* triplet photo-

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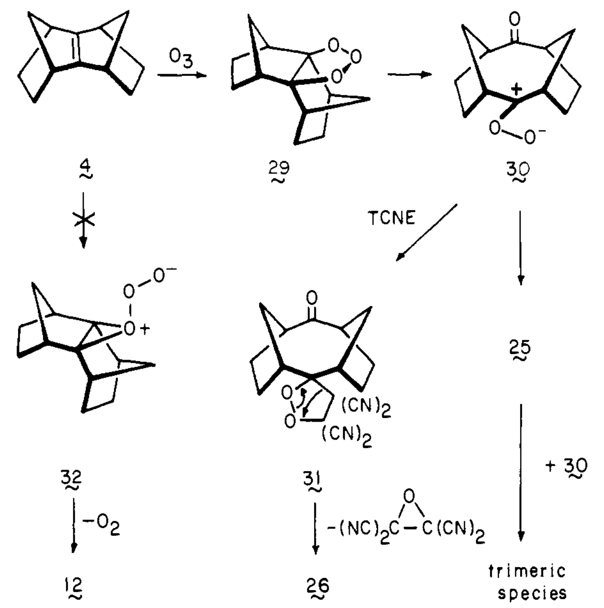
(24) Cremer, D. *J. Chem. Phys.* **1979**, *70*, 1898, 1911, 1928.

(25) Keul, H. *Chem. Ber.* **1975**, *108*, 1198, 1207.

(26) Jefford, C. W.; Boschung, A. F. *Tetrahedron Lett.* **1976**, 4771.

Scheme II



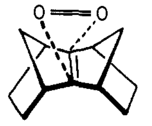
sensitizers benzil and biacetyl resulted in efficient epoxidation.[27] However, singlet oxygen was considered not to be involved in these reactions because of the lack of most of the products characteristic of olefin-$^1O_2$ chemistry.

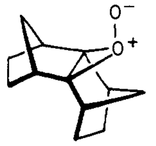
Discussion

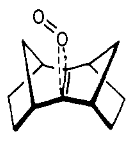
Despite the sterically hindered nature of the central double bond in **5** and **6**, these molecules capture triplet oxygen with unparalleled facility to give well-defined oxidation products. Whereas it is adequate simply to expose **6** to air to achieve rapid epoxidation, **5** gives rise to exo epoxide **19** and diketone **20** in a slower autoxidation process. The data require that several constraints be placed on any hypothetical mechanism. First, one or more intermediates must be able to lead directly or indirectly to epoxide and diketone products. Furthermore, the inhibitor experiments suggest that a radical chain process may be involved and therefore that a cycle of chain-propagating steps probably intervenes. The formation of mixtures of epoxides and carbonyl compounds upon *radical-initiated* autoxidation of much simpler olefins lacking reactive allylic hydrogens is known and the mechanism appears to be well established.[28] What is noteworthy in the present instance is the low-temperature spontaneous initiation. The manner in which initiation occurs is, of course, speculative. Possibilities include initial corner π-bond attack by $^3O_2$ to give a biradical or electron-transfer leading to superoxide. In the first instance, biradical closure would generate an energetic dioxetane whose ensuing exothermic cleavage to diketone would be anticipated. An alternative reaction channel available to the same intermediate is dimerization to give a carbon-centered biradical whose collapse could yield either a dioxetane or 2 mol of epoxide and an oxygen molecule. Not adequately addressed by either of these proposals is the question of chain propagation. Although the precise details by which this phenomenon operates are not known, the inhibitor must act very early since epoxide and diketone production are both affected (Table I).

A satisfactory plausible mechanism for the ozonolysis of **4** involves initial 1,3-dipolar cycloaddition of ozone to deliver the primary ozonide **29** (Scheme II). This event conforms to the reaction course followed by phenyl azide and provides a reactive intermediate whose structural type enjoys literature precedent.[30] Considerable strain relief can be achieved within **29** by fragmentation to the carbonyl oxide **30** which simply dimerizes to the diperoxide **25** (likely a stereoisomeric mixture) in pentane or ethyl acetate solution. The interception of **30** was successfully achieved upon addition of TCNE. In agreement with earlier observations of a similar nature,[25,31] TCNE enters into efficient 1,3-dipolar cycloaddition with **30** to provide dioxalane adduct **31** which subsequently collapses to diketone **26** and TCNE oxide. The absence of epoxide **12** tacitly argues against the initial formation or subsequent involvement of peroxy epoxide **32**.

The rigid structural framework of **4** is expected to preclude the possibility of $(\pi^2s + \pi^2a)$ cycloaddition with singlet oxygen as in **33**. Despite this, **4** is slowly converted to diketone **26** in a process presumably mediated by a dioxetane. This behavior contrasts with the singular inability of anti isomer **7** to provide any trace of dioxetane or of products derived therefrom.[6] The substantially lowered reactivity of **4**, atypical for a tetrasubstituted ethylene and especially so for a π bond having heightened electron-donor character (8.27 eV), is believed to be primarily due to steric factors. It is particularly attractive to consider inhibition of a normally favored $(\pi^2s + \pi^2a)$ approach. Notwithstanding, reaction does proceed. Perhaps $^1O_2$ capture is achieved by means of (2 + 1) cycloaddition which initially delivers perepoxide **34**. This mechanism also requires the electrophilic oxygen species to approach in a plane perpendicular to the C═C bond. However, the end-on angle required to arrive at **34** (viz. **35**) is less spatially demanding than the mutually coplanar transition state involved in direct dioxetane production (i.e., **35**). Perepoxide **34** should be unstable relative to the dioxetane into which it can isomerize by conventional electronic reorganization.


33


34


35

As in preceding studies,[32] we consider epoxide production which surfaces in the rose bengal experiments not to be the direct result of a singlet oxygen reaction but to originate from extraneous intermediates generated by the sensitizer.

In summary, the uniquely structured molecules **4–6** have been shown to offer a richly varied spectrum of reactivity toward various oxygenating agents. In reactions involving corner or parallel-plane attack on the central double bond, steric hindrance to exo capture does not appear to be inhibitory. In customary fashion, singlet oxygen has proven particularly sensitive to the congestion present in these molecules. The existing dichotomy in the reactivity of **4** and **7** is believed by us to be a reflection of the fact that, while capture of an electrophile by **4** proceeds exo to both norbornyl segments, an exo–endo stereocombination is required in the case of **7**. The usual consequences of endo bonding to norbornyl rings, whether totally steric or partially electronic, must be given due to consideration. Perhaps work currently in progress in The Ohio State and The Texas Christian University laboratories will shed light on this question.

Experimental Section

Melting points are uncorrected. Proton magnetic resonance spectra were obtained with Varian T-60 and Bruker HX-90 spectrometers; apparent splittings are given in all cases. Carbon spectra were recorded on the Bruker unit. Infrared and mass spectra, the latter at an ionization potential of 70 eV, were determined on Perkin-Elmer Model 467 and AEI-MS9 spectrometers, respectively. Elemental analyses were per-

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(29) Hydroxyl radicals are recognized to be generated under the conditions of the Fenton reaction. Generally speaking, ·OH reacts with organic substrates either by hydrogen abstraction or by addition to an unsaturated system. For recent discussions, consult: (a) Nonhebel, D. C.; Tedder, J. M.; Walton, J. C. "Radicals"; Cambridge University Press: New York, 1979. (b) Kochi, J. K. "Free Radicals"; Wiley: New York, 1973.

(30) Consult ref 21, Chapter 4, for relevant references on this topic.

(31) (a) Criegee, R.; Günther, P. *Chem. Ber.* **1963**, *96*, 1564. (b) Griesbaum, K.; Brüggemann, J. *Adv. Chem. Ser.* **1972**, *No. 112*, 50; *Chem. Ber.* **1972**, *105*, 3638. (c) Griesbaum, K.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 2877. (d) Gozzo, F.; Camaggi, G. *Chim. Ind.* (*Milan*) **1968**, *50*, 197.

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formed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***syn*-1,2,3,4,5,6,7,8-Octahydro-1,4:5,8-dimethanonaphthalene (4).** A solution of isodicyclopentadiene (5.7 g, 43 mmol) and phenyl vinyl sulfone (7.5 g, 43 mmol) in 20 mL of dichloromethane was heated at reflux under argon for 16 h. The cooled solution was evaporated, and the residue was chromatographed on silica gel (300 g). Elution with 15% ethyl acetate in hexane afforded 11.7 g (90.7%) of the endo adduct with an exo phenylsulfonyl group as a colorless solid: mp 136–137 °C (from 15% ethyl acetate in hexane); IR (CCl_4) 3020, 2990, 2945, 1320, 1145 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.04–7.38 (m, 5 H), 3.33 (br s, 1 H), 2.96 (m, 4 H), 2.62 (ddd, J = 8.5, 4.0, 1.5 Hz, 1 H), 2.27–0.42 (series of m, 9 H); mass spectrum *m/e* calcd 300.1184, obsd 300.1190.

Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.97; H, 6.71. Found: C, 71.88; H, 6.71.

Into anhydrous methanol (40 mL) containing disodium hydrogen phosphate (3.2 g, 27 mmol) and 6% sodium amalgam (8.3 mg-at of Na) was introduced a solution of the above sulfone (900 mg, 3.0 mmol) in 10 mL of tetrahydrofuran. The mixture was stirred at room temperature for 2.5 h under argon, at which point pentane (40 mL) and water (50 mL) were added. The layers were separated and the pentane fraction was washed with water (3 × 20 mL), dried, and evaporated. Elution of the residue through a small amount of basic alumina (pentane elution) furnished 410 mg (85%) of **4** as a colorless waxy solid: mp 33–34 °C; IR (neat) 2972, 2928, 2898, 2875, 1480, 1462, 1447, 1385, 776 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.91 (m, 4 H), 1.67–0.57 (series of m, 12 H); ^{13}C NMR ($CDCl_3$) 151.6, 50.3, 42.9, 25.3 ppm; mass spectrum, *m/e* calcd 160.1252, obsd 160.1255.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.84; H, 10.02.

Competitive Epoxidation of 4 and 5. A cold (−20 °C) solution of **4** (50 mg, 0.31 mmol) and **5**[5] (65 mg, 0.31 mmol) in dichloromethane (5 mL) was treated dropwise with a solution of *m*-chloroperbenzoic acid (52 mg, 0.25 mmol) in the same solvent (5 mL). After 25 min, thin-layer chromatographic (TLC) analysis on silica gel (elution with 10% ethyl acetate in hexane) indicated the presence of **19** but no **12**.[10] Following workup, ^1H NMR analysis of the unpurified residue indicated **4** and **5** to be present in the approximate ratio of 5:1. The epoxide signals were not sufficiently clear for ratio determination. The complete characterization of **19** is reported below.

Autoxidation of 5. Dry oxygen was bubbled through a solution of **5** (4.8 g, 23 mmol) in benzene (15 mL) for 48 h. The solution was filtered through 60 g of silica gel (elution with 10% ethyl acetate in hexane) and 2.49 g (48%) of epoxide **19** was obtained. Continued elution with 40% ethyl acetate in hexane gave 2.09 g (38%) of diketone **20**.

For **19**: mp 89–90.5 °C (from ethanol); IR (CCl_4) 3070, 3045, 2980, 992 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35–6.8 (m, 4 H), 3.42 (br s, 2 H), 2.8–0.3 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) 150.48 (s), 125.35 (d), 122.94 (d), 63.96 (s), 53.81 (t), 46.75 (d), 40.54 (d), 38.83 (t), 26.22 (t) ppm; mass spectrum, *m/e* calcd 224.1201, obsd 224.1208.

Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.52; H, 7.30.

For **20**: mp 148.5–149.5 °C (from ethyl acetate–hexane, 1:3); IR (CCl_4) 3065, 2955, 1684, 1250, 1132, 842 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20 (br s, 4 H), 4.25 (dd, J = 5.5, 4.5 Hz, 2 H), 3.15 (m, 2 H), 2.70 (br d, J = 4.5 Hz, 2 H), 2.20 (m, 4 H), 1.42 (br d, J = 5.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 211.2, 142.9, 128.9, 125.4, 59.4, 54.2, 33.1, 31.3, 28.6 ppm; mass spectrum, *m/e* calcd 240.1150, obsd 240.1158.

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.94; H, 6.71.

Cycloaddition of Isodicyclopentadiene and Dimethyl Acetylenedicarboxylate. Direct Conversion of Adduct 6 to Epoxide 21. A solution of isodicyclopentadiene (1.8 g, 13.8 mmol) in 10 mL of dichloromethane was added dropwise to a cold (<5 °C) solution of dimethyl acetylenedicarboxylate (1.8 g, 12.7 mmol) in the same solvent (5 mL). The reaction mixture was stirred under nitrogen for 1 h. The yellow solution was evaporated, and the ^1H and ^{13}C NMR spectra were immediately recorded: ^1H NMR ($CDCl_3$) δ 6.30 (A_2B_2, 2 H), 3.78 (s, 6 H), 3.53 (m, 4 H), 2.47–1.95 (m, 4 H); ^{13}C NMR ($CDCl_3$) 173.0, 166.0, 152.0, 139.8, 68.9, 65.8, 53.8, 51.9, 50.3 ppm.

Oxygen was then admitted to the yellow solution for 10 min via a pipet which extended to the bottom of the flask. The flask was stoppered and stirred for 10 min. The crude product was submitted to preparative thin-layer chromatography on silica gel (50% ethyl acetate in hexane) and the least polar band (R_f = 0.6) was collected to give 2.35 g (59%) of **21** as a clear viscous liquid: ^1H NMR ($CDCl_3$) δ 6.12 (A_2B_2, 2 H), 3.77 (s, 6 H), 3.27 (m, 2 H), 3.05 (m, 2 H), 2.18 (m, 2 H), 1.58 (dt, J = 8.5, 1.5 Hz, 1 H), 1.28 (dt, J = 8.5, 2.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 164.7, 150.9, 141.5, 75.0, 52.4, 52.0, 51.2, 49.3, 45.8 ppm; mass spectrum, *m/e* calcd 288.0998, obsd 288.1005.

Photocyclization of 21. A solution of **21** (280 mg, 0.97 mmol) in 12 mL of acetone contained in a Pyrex test tube was irradiated with a bank of 3500-Å lamps in a Rayonet reactor for 2.5 h. The solvent was evaporated, and the product was purified by preparative TLC on silica gel (elution with ethyl acetate–hexane, 3:2) to give 217 mg (77.5%) of **22** as a colorless crystalline solid: mp 88.5–89.5 °C (from ether–hexane); IR (CCl_4) 2960, 2935, 1737, 1425, 1220, 841 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.63 (s, 6 H), 2.93 (dd, J = 3.0, 1.8 Hz, 2 H), 2.58 (m, 2 H), 2.43 (m, 2 H), 1.87 (d with fine splitting, J = 3.0, 1.8 Hz, 2 H), 1.53 (d with fine splitting, J = 7.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 172.2 (s), 62.9 (s), 59.4 (s), 51.96 (q), 43.57 (d), 41.82 (d), 39.02 (d), 34.52 (t), 33.47 (t) ppm; mass spectrum, *m/e* calcd 288.0998, obsd 288.1005.

Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.56; H, 5.59. Found: C, 66.66; H, 5.59.

Ozonolysis of 4. Into 150 mL of pentane (or ethyl acetate) was dissolved 285 mg (1.78 mmol) of **4**. The solution was cooled in a dry ice–acetone bath, and ozone was admitted until the blue color persisted. The powdery white precipitate was collected by filtration and dried in vacuo to give 315 mg (85%) of **25**: mp >160 °C dec; IR (CCl_4) 2980, 2945, 1677, 1468, 1032 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.72–0.83 (series of m); ^{13}C NMR ($CDCl_3$) 215.4, 110.4, 54.0, 31.42, 29.90, 25.90 ppm; field desorption mass spectrum, *m/e* 417 (M^+ + 1). This spectrum also indicated the presence of a small amount of a trimeric substance, *m/e* 625 (M^+ + 1).

Hydrogenation of 25. Conversion to Diketone 26. A mixture of platinum oxide (12 mg) and ethanol (12 mL) was prereduced at atmospheric pressure for 5 min and then cooled to −45 °C. A solution of **25** (72 mg, 0.173 mmol) in ethanol (5 mL) was added, and the suspension was stirred under a hydrogen atmosphere for 3 h. The catalyst was removed by filtration through Celite, the filtrate was evaporated, and the residue was passed through a short column of silica gel (10 g, elution with ethyl acetate–hexane, 2:1). There was isolated 37 mg of a pale tan solid which proved in all respects identical with an authentic sample of diketone **26** (see below).

Ozonolysis of 4 in the Presence of Tetracyanoethylene. A solution containing 0.50 g (3.13 mmol) of **4** and 0.40 g (3.13 mmol) of freshly sublimed TCNE in 80 mL of ethyl acetate was cooled to −78 °C, and ozone was admitted until the blue color persisted. The clear solution was evaporated to leave a yellow residue, the ^{13}C NMR spectrum of which showed it to consist of **26** and TCNE oxide. This product was filtered through a short column of silica gel as above and 485 mg (81%) of the diketone was isolated as a colorless crystalline solid: mp 194 °C (after sublimation at 120 °C (0.1 torr)); IR (CCl_4) 2960, 2935, 2875, 1678, 1475, 1280 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.52–3.01 (br m, 4 H), 3.02 (br d, J = 15.2 Hz, 2 H), 2.47–1.46 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) 214.4, 54.6, 31.5, 31.3 ppm; mass spectrum, *m/e* 192 (M^+).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.76; H, 8.36.

Cycloaddition of Phenyl Azide to 4. A solution of **4** (320 mg, 2.0 mmol) and phenyl azide (240 mg, 2.02 mmol) in 5 mL of ethyl acetate was allowed to stand at room temperature for 4 h. Hexane (5 mL) was added and 355 mg of clear-white prisms crystallized. Processing of the mother liquor afforded an additional 117 mg of **27** (total yield, 85%): mp 135–136 °C; IR (CCl_4) 3050, 3018, 2980, 2942, 2137, 1600, 1495, 1480, 1440, 1340, 1042 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22 (m, 2 H), 6.55–6.32 (m, 3 H), 2.87 (m, 2 H), 2.60 (m, 2 H), 2.4–0.92 (series of m, 12 H); mass spectrum, *m/e* 251 ($M^+ - N_2$).

Photolysis of 27. A solution of **27** (95 mg, 0.34 mmol) in 7 mL of acetone was placed in a Pyrex test tube and irradiated with a bank of 3500-Å lamps in a Rayonet reactor for 1 h at which time nitrogen evolution had ceased. The solvent was evaporated to leave 81 mg (95%) of tan solid. This material was sublimed at 100–105 °C (0.5 torr) to give pure **28** as a white solid: mp 106.5–108 °C; IR (CCl_4) 3040, 2960, 2880, 1598, 1501, 1413, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.20–6.27 (series of m, 5 H), 2.74 (m, 4 H), 2.25–1.30 (series of m, 10 H), 0.72–0.53 (m, 2 H); ^{13}C NMR ($CDCl_3$) 150.3 (s), 129.7 (d), 116.3 (d), 112.6 (d), 41.9 (t), 41.9 (d), 27.4 (t) ppm; mass spectrum, *m/e* calcd 251.1674, obsd 251.1680.

Anal. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.42. Found: C, 86.05; H, 8.45.

Rose Bengal-Sensitized Photooxygenation of 4. Into an immersion jacket fitted with a glass frit at its base was placed 2.31 g (14.4 mmol) of **4**, 1.8 g of Photox (polymer bound rose bengal), and 220 mL of dry benzene. The solution was irradiated for 80 h with a Sylvania 500-W DYV tungsten halogen lamp while oxygen was bubbled through the solution. The polymer was removed by filtration, the solvent was evaporated, and the residue was chromatographed on silica gel (50 g). Elution with hexane furnished 140 mg (6.1%) of recovered **4**. Continued elution with 10% ethyl acetate in hexane gave 650 mg (26%) of epoxide **12** which was further purified by sublimation at 60 °C (0.1 torr) and obtained as

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a white solid: mp 88-89 °C; IR (CCl$_4$) 3020, 2960, 1466, 1295 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.72 (m, 4 H), 2.08-1.32 (series of m, 10 H), 0.68 (br d, J = 8.5 Hz, 2 H); ^{13}C NMR (CDCl$_3$) 58.6 (s), 41.1 (d), 38.9 (t), 27.1 (t) ppm; mass spectrum, m/e calcd 176.1201, obsd 176.1206.

Anal. Calcd for C$_{12}$H$_{16}$O: C, 74.97; H, 8.39. Found: C, 74.76; H, 8.36.

Further elution with 45% ethyl acetate in hexane yielded 1.62 g (59%) of diketone **26**.

Methylene Blue-Sensitized Photooxygenation of 4. A solution of **4** (910 mg, 5.69 mmol) and methylene blue (110 mg, 2.7 mmol) in 110 mL of dry acetonitrile (distilled from CaH$_2$) was irradiated in the above manner for 65 h while oxygen was continuously introduced through a frit in the base of the reaction vessel. The solvent was evaporated, and a portion of the residue was taken up in CDCl$_3$ and its ^{1}H and ^{13} NMR spectra were recorded. The reaction was found to be 30% complete with diketone **26** present as the only product. TLC analysis also indicated the absence of epoxide. The combined residue was dissolved in dichloromethane (5 mL) and filtered through silica gel (15 g) with pentane to remove unreacted **4** (485 mg). Further elution with 70% ethyl acetate in hexane afforded 204 mg of **26** as a white solid, in all respects identical with authentic material.

Tetraphenylporphin-Sensitized Photooxygenation of 4. A solution of **4** (830 mg, 5.19 mmol) and tetraphenylporphin (115 mg) in 100 mL of 1,2-dichloroethane (distilled from Na$_2$CO$_3$) was irradiated in the prescribed manner for 76 h. The solvent was evaporated, and the spectra of the residue were recorded. These data and the subsequent isolation only of **26** served to indicate that only diketone had been formed.

Acknowledgment. We are grateful to the National Cancer Institute (Grant CA-12115) for financial support and to Dr. Richard Eizember (Eli Lilly Co.) for the field desorption mass spectrum of **25**.

Dioxygen Transfer from 4a-Hydroperoxyflavin Anion. 3. Oxygen Transfer to the 3-Position of Substituted Indoles

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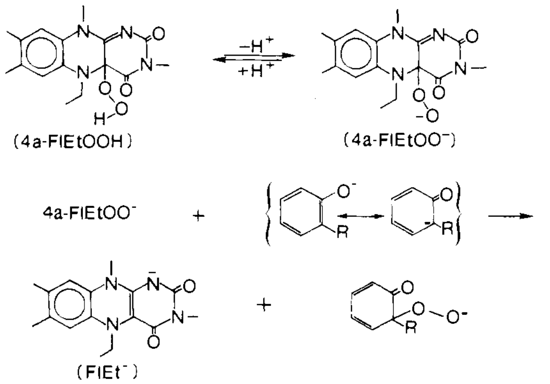
Received May 27, 1980

Abstract: The 4a-hydroperoxyflavin anion (4a-FlEtO$_2^-$) spontaneously decays with a rate constant of 4.2 × 10^{-2} s^{-1} (*tert*-butyl alcohol, 30 °C). In the presence of the anions of 2,3-dimethylindole (**1a**$^-$) and 5-methoxy-3-methyl-2-phenylindole (**2a**$^-$) the pseudo-first-order rate constants (k_{obsd}) for disappearance of 4a-FlEtO$_2^-$ increase. Plots of $1/k_{\text{obsd}}$ vs. $1/[\mathbf{1a}^-]$ and $1/[\mathbf{2a}^-]$ are linear, and the limiting rate constants for 4a-FlEtO$_2^-$ disappearance at high values of [**1a**$^-$] and [**2a**$^-$] were calculated, from the intercepts, to be 0.33 and 0.37 s^{-1}, respectively. In a previous study the limiting rate constants were 0.36 and 0.37 s^{-1} when the anions of 2,6-di-*tert*-butyl-4-methylphenol and 3,5-di-*tert*-butylcatechol were employed. This limiting rate constant of 0.36 s^{-1} is assigned as the forward rate for the conversion of 4a-FlEtO$_2^-$ (in an endothermic equilibrium) to a species (X) which, on being trapped by substrate anion, transfers a peroxy moiety to the trapping agent. The yields of the dioxygen-transfer products formed from **1a**$^-$ and **2a**$^-$ are 24% and 41%, respectively. The singlet oxygen-trapping agents, 2,5-dimethylfuran and tetramethylethylene, do not increase the rate of disappearance of 4a-FlEtO$_2^-$ and, therefore, do not trap X. Species X cannot be solvent separated ^{1}O$_2$ and FlEt$^-$. Moreover, the rate constants for reaction of triplet oxygen with **1a**$^-$ and **2a**$^-$ are 10^3-10^4 too small for X to be solvent separated ^{3}O$_2$ and FlEt$^-$. The possibility of X being solvent separated FlEt· and O$_2^-$· is considered. Possible identities for X include a complex of an oxygen and a flavin species and a 4a,10a-dioxetane of reduced flavin.

In parts 1 and 2 of the present study, it was established that the 4a-hydroperoxyflavin anion (4a-FlEtOO$^-$) transfers a dioxygen species to a number of ambident phenolate anions (eq 1).[1,2] The products realized from the peroxidized substrate are very dependent upon their structure (for example, eq 2-4). Regardless of the nature of the phenolate anion employed, dioxygen transfer proceeds only after the conversion of 4a-FlEtO$_2^-$ to an intermediate



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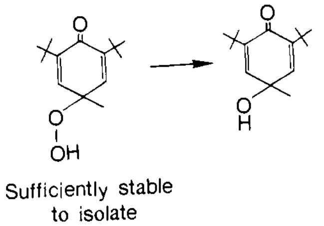

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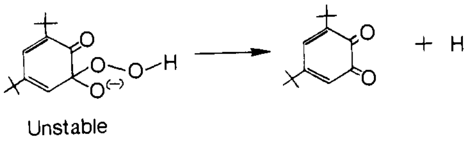

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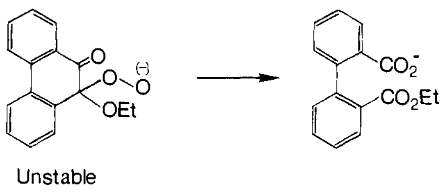

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[1] Kemal, C.; Bruice, T. C. *J. Am. Chem. Soc.* **1979**, *101*, 1635.
[2] Muto, S.; Bruice, T. C. *J. Am. Chem. Soc.* **1980**, *102*, 1465.