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Reaction of Singlet Oxygen with 2-Methylnorbornadiene and 2-Methylidenenorbornene. Evaluation of Electronic and Steric Effects on the Course of Hydroperoxidation

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Received August 30, 1977

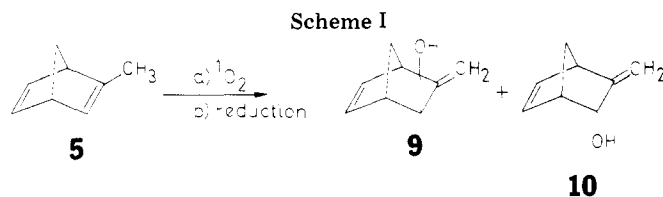
The dye-sensitized photooxygenation of 2-methylnorborna-2,5-diene (**5**) and 2-methylidenenorborn-5-ene (**6**) has been studied. Olefin **5** gave the expected allylically rearranged *exo* and *endo* hydroperoxides in a ratio of 7.3:1. Olefin **6** gave the allylically rearranged hydroperoxide (98%) together with the *exo* and *endo* epoxides deriving from the methyldiene function (2%). The rates of photooxygenation of **5** and **6** were compared with those obtained with 2-methylnorborn-2-ene (**1**), 2-methylidenenorbornane (**2**), 1-methylcyclopentene (**7**), and methyldienecyclopentane (**8**). The partial rates for oxygen attack on the *exo* faces of the bicyclic olefins were found to parallel the ionization potentials of the reacting double bonds. An interpretation of electronic and steric effects was made in terms of the formation of an activated complex arising from the interaction of the HOMO of the olefin with the LUMO of singlet oxygen.

Norbornene is a substrate par excellence for the study of the mechanism of reactions occurring at the double bond. Norbornene itself is slowly oxidized by singlet oxygen, but cannot give hydroperoxide in an *ene*-type reaction as the allylic carbon-hydrogen bond lies in the nodal plan of the double bond.¹ However, 2-methylnorbornene (**1**) and 2-methylidenenorbornane (**2**) react readily to give the allylic hydroperoxides.²

Compounds **1** and **2**, unlike simple olefins, only undergo the "ene" reaction in one direction. Furthermore, the approach of the oxygen molecule is differentiated by the *exo* and *endo* faces of the norbornyl skeleton. By studying rates of photooxygenation and product analyses of **1** and **2** together with their 7,7-dimethyl derivatives **3** and **4** (Table I) we discovered that, while the *endo* sides in the series **1**-**4** are really indistinguishable, the partial rates for the *exo* side varied significantly.³

The presence of methyl at C(7) depressed the rate of attack by oxygen much more at an internal than an external double bond. We concluded that steric hindrance in the ground-state structures is an important rate-determining factor for the hydroperoxidation reaction. We deduced that steric strictures operate in the formation of the carbon-oxygen bond, but not in the abstraction of the allylic hydrogen atom, and further that the former event precedes the latter. As a consequence the transition state should have dipolar character; partial negative charge would accumulate on the terminal oxygen atom counterbalancing positive charge dispersed hyperconjugatively over the allylic portion (Figure 1). There are two important corollaries, if this picture is correct. The first is that when steric and statistical differences are negligible for a pair of competing "ene" modes, then the products should be partitioned according to the relative importance of the Markownikoff effects. The second is that, as oxygen behaves as an electrophile, rates ought to be determined by the relative energies of the respective frontier orbitals.

In this paper we examine the validity of this second corollary by modifying the molecular orbital levels of the reacting olefin by introducing a second double bond, but which is essentially inert to singlet oxygen. The substrates chosen are



2-methylnorbornadiene (**5**) and 2-methylidenenorbornene (**6**). The kinetics and stereochemistry of the photooxygenation of **5** and **6** are compared with the monoolefinic parents **1** and **2** together with the monocyclic olefins, 2-methylcyclopentene (**7**) and 2-methyldienecyclopentane (**8**).

Results

Product Analyses. Photooxygenation of 2-methylnorbornadiene gave, after reduction with triphenylphosphine or sodium borohydride, a mixture of the expected *exo* and *endo* allylic alcohols **9** and **10** in a ratio of 7.33:1 in a yield of 88% (Scheme I).

2-Methylidenenorborn-5-ene (**6**) under similar conditions gave the expected hydroperoxymethyl derivative **11**. However, the *exo*- and *endo*-epoxides **12** and **13** were also obtained together with traces of norborn-2-en-2-one (**14**) (Scheme II). As the photooxygenation leading to primary products was slow, the reaction was stopped after 2% conversion of **6**; the relative percentages of the products so obtained were 98% (**11**), 0.2%

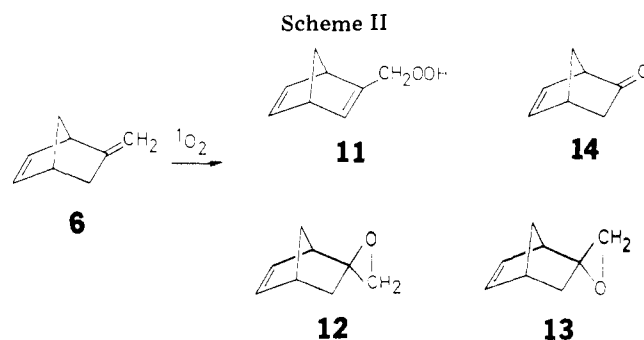
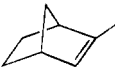
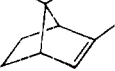
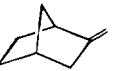
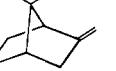


Table I. Relative Rates of Photooxygenation of 2-Methylnorbornene, 2-Methylidenenorbornane, and Their 7,7-Dimethyl Derivatives

				
	1 ^a	3 ^b	2 ^c	4 ^d
$k_{rel}(\text{total})$	40.0	1.0	13.0	3.4
$k_{rel}(\text{exo})$	39.4	0.16	12.5	1.4
$k_{rel}(\text{endo})$	0.6	0.84	0.5	2.0

^a Registry no. 694-92-8. ^b Registry no. 514-14-7. ^c Registry no. 497-35-8. ^d Registry no. 471-84-1.

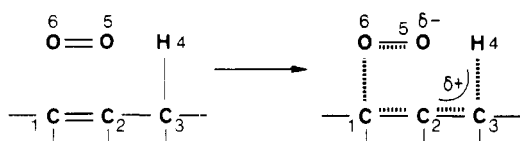
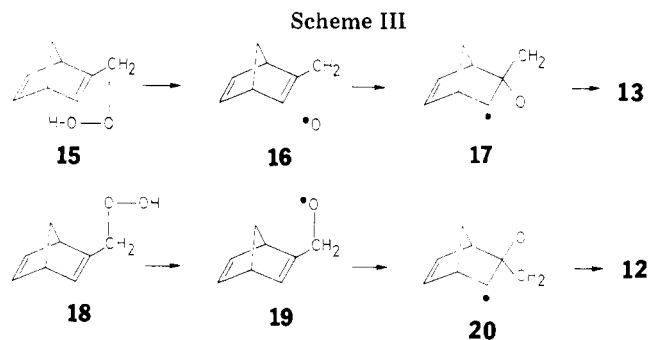


Figure 1. Creation of dipolar transition state leading to allylicly rearranged hydroperoxide.

(12), and 1.8% (13). The assignment of structures to 12 and 13 was made by comparison with authentic samples prepared independently.⁴

No equilibration between 12 and 13 occurred under the conditions of gas-phase chromatography. Moreover, the ratio was invariant with the amount of 6 consumed and therefore it can be assumed that they arise from secondary reactions of hydroperoxide 11. This assumption was confirmed by irradiating 11 under nitrogen instead of oxygen. A mixture of the 13 and 12 epoxides was obtained in a ratio of 5.6:1. The predominance of the endo isomer (13) can be attributed to the preferred conformation of the hydroperoxide in which the hydroxy grouping points toward the endo side of the diene moiety (15). This conformation should be favored over others, e.g., 18, by virtue of intramolecular hydrogen bonding. Homolysis of the oxygen-oxygen bond in 15 will furnish the oxy radical 16 which on rapid closure gives the homoallylic radical 17, whence 13 (Scheme III). In similar fashion, the less favored



conformational isomer 18 generates the radicals 19 and 20, which furnish the *exo*-epoxide 12.

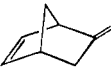
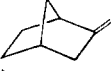

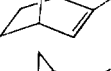
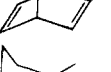
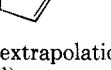
Kinetics. The total rates of photooxygenation of the six olefins were determined by measuring the disappearance of substrate. For the purposes of comparison, rates were partitioned into relative rates for *exo* and *endo* attack. As the products resulted from kinetic control, the *exo/endo* isomer ratio gives the partial rates directly. The *exo/endo* ratio for 6 was estimated by assuming that the proportionality which pertains to the pair of olefins 1 and 2 also holds for the pair 5 and 6 (Table II).

Discussion

On inspecting Table II, it is seen that the monocyclic olefins react faster than their bicyclic counterparts. There also appears to be an inconsistency for the bicyclic partners. On going from the norbornene 1 to the norbornadiene 5, the rate increases some 2.5 times, whereas on passing from the norbornane 2 to the norbornene 6 the rate actually decreases fourfold. These different rates can be usefully analyzed by considering the frontier orbitals of the reactants.

The approach of the singlet oxygen molecule to the olefin will result in a mutual perturbation of the appropriate frontier orbitals.^{6,7} Two limiting approaches may be considered. In the first, the whole allylic fragment is attacked by both ends of the oxygen molecule; an *ene*-type mechanism operates and the hydroperoxide is formed with allylic shift (Figure 2a). In the second, the oxygen molecule adds end-on to the double bond creating a perepoxide, which subsequently rearranges to the allylic hydroperoxide (Figure 2b). Since oxygen is an electrophile, the dominant interaction will be that between the lowest unoccupied molecular orbital (LUMO) of oxygen and

Table II. Relative Rates of Photooxygenation of Some Cyclic Monoolefins Together with Their Ionization Potentials

No.	Substrate	Registry no.	Exo/endo isomer ratio	k_{rel} (total)	k_{rel} (exo)	k_{rel} (endo)	k_{rel} (exo')	ln k_{rel} (exo')	IP, eV
6		694-91-7	3.0 ^a	1	0.75	0.25	1	0	9.31 ^c
2			28 ^b	4.3	4.15	0.15	5.5	1.7	9.02 ^c
8		1528-30-9	1	15.5	7.75	7.75	10.3	2.33	9.15 ^d
1			66 ^b	13.5	13.3	0.2	17.7	2.87	8.57 ^e
5		5235-55-2	7.3	34.0	30	4	40.0	3.69	8.42 ^c
7		693-89-0	1	507	253	253	338	5.82	8.55 ^d

^a By extrapolation, see text. ^b Obtained from ref 1 and 3. ^c Obtained from ref 5. ^d See ref 23. ^e Determined by E. Haselbach (University of Basel).

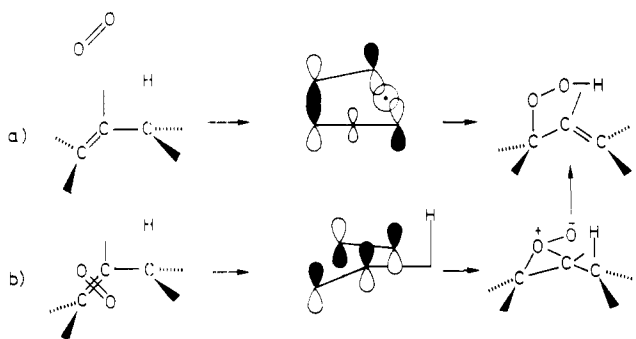


Figure 2. Alternative transition states leading to allylic hydroperoxidation. (a) The concerted ene reaction. (b) Cheletropic reaction generating transient peroxide.

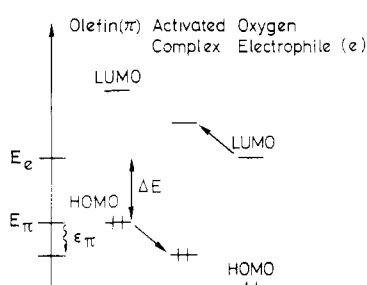


Figure 3. Interaction of the HOMO of the olefin with the LUMO of singlet oxygen to form the activated complex.

the highest occupied molecular orbital (HOMO) of the allylic or, to simplify matters, the double bond portions respectively (Figures 2a and 2b).⁸⁻¹⁰

The stabilization (ϵ_π) attained on forming the activated complex will be a linear measure of the rate of reaction.

$$\text{rate} = f(\epsilon_\pi), \epsilon_\pi = -\mathcal{H}^2/\Delta E$$

Moreover, the extent of the lowering of the HOMO level (ϵ_π) of the olefin is determined by the closeness of the energy gap (ΔE) existing between the respective orbitals of the olefin (E_π) and oxygen (E_e) before interaction (Figure 3). The numerator of the perturbation expression also shows that the size of the stabilization depends on the square of the hamiltonian (\mathcal{H}), namely on the matching of symmetries and the overlap capabilities of the interacting orbitals. For practical purposes, ionization potentials (IP) and electron affinities (EA) can represent the energies of the HOMO and LUMO levels, respectively.^{11,12}

$$\text{rate} \propto \mathcal{H}^2/[\text{IP}_{\text{HOMO}} - \text{EA}_{\text{LUMO}}] \quad (1)$$

As oxygen is used throughout, the value of its electron affinity is not needed. Assuming that the numerator of eq 1 is constant for a series of olefins, their ionization potentials should constitute a reliable index of their rates of photooxygenation. As we shall see later, the application of this empirical expression furnishes information on electronic and steric effects.

For the bicyclic dienes, a sizable splitting exists between the pairs of ionization potentials, 0.38 eV for 6 and 0.68 eV for 5, indicating a strong interaction between the homoconjugated orbitals.¹³ Although the systems themselves are not appreciably stabilized, the reactivity of the allylic double bonds is significantly altered. When two doubly occupied molecular orbitals interact, the lower-lying level is stabilized while the higher is destabilized, the effect being greater the closer the levels in energy.¹⁴ Accordingly, the experimental ionization potentials can be assigned to each of the homoconjugated double bonds (π_A and π_B) (Table III). Since it is only the allylic fragment (which contains π_B) which can react, the fron-

Table III. Ionization Potentials and Electron Densities of Norbornane-Type Olefins

Olefin	Electron density ^a		IP obsd, eV	
	π_A	π_B		
2		1.33	9.02	
6		1.28	0.14	8.93
6		0.15	1.28	9.31
1		1.40	8.57	
5		0.19	1.41	8.42
5		1.35	0.23	9.10
5		1.40	8.97 ^b	

^a Calculated by MINDO/3. ^b Reference 14a.

tier orbital implicated in the reaction will be the HOMO for 5, but the next HOMO for 6. For the bicyclic series the denominator of eq 1 is a minimum for 5 and a maximum for 6, so that the reactivity rates (k) should increase in the order

$$k_6 < k_2 < k_1 < k_5$$

which is in fact the case.

Strictly speaking, the numerator also affects the rate; however, MINDO/3 calculations indicate, notwithstanding their drawbacks, that the electron densities in the π_B part are relatively unchanged for the pairs 1/5 and 2/6 (Table III). The calculations are less than satisfactory for the IP's, but this is less important, as the experimental values are available. Therefore, for each pair, the numerator of eq 1 remains the same.

Nevertheless, discrepancies in the rates still remain. The sequence of ionization potentials certainly parallels the rates found for the bicyclic olefins, but for a constant IP the methyldene derivatives react faster than their endocyclic isomers. Moreover, the monocyclic reference compounds react even faster still, much more so than their ionization potentials would indicate. A way of reconciling these differences is to assume that the simplest structures, the references 7 and 8, are reacting normally and that photooxygenation of the bicyclic olefins is sterically retarded.

A semiquantitative measure of steric effects is obtainable by plotting the logarithm of rates against ionization potentials, or rather the logarithms of the exo partial rates, assuming the exo faces of the substrates to have more in common topographically than the endo faces. If it is assumed that for each pair of olefins (7/8, 2/6, and 1/5) the exo steric environment is the same, then three parallel straight lines are obtained (Figure 4). Olefins 7 and 8 are conformationally mobile and thus the fit of both partners in the activated complex is as good as it can be. However, on passing to the rigid methyldene derivatives, 2/6, approaching oxygen now experiences hindrance by the C(7) syn hydrogen atom (Figure 5); the fit is less good and

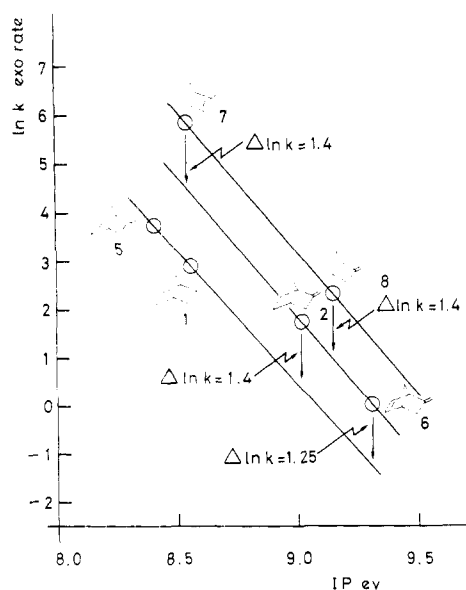


Figure 4. Correlation of the rate of exo photooxygenation with the ionization potential of the reacting double bond (π_B) for some cyclic and bicyclic olefins.



Figure 5. Different steric impediments due to the C(7) *syn*-hydrogen atom experienced by oxygen approaching (a) the midpoint of an external double bond and (b) an internal double bond in the norbornane-type skeleton.

the depression in rate of $\Delta \ln k \sim 1.4$ is about the same for both. If the oxygen is obliged to insert itself deeper into the bicyclic skeleton (Figure 5), as is the case for the pair of norbornenes 1/5, the extra hindrance arising from the C(7) hydrogen atom occasions a further slowing in rate of about $\Delta \ln k \sim 1.25$ –1.4. This steric trend is corroborated by the exo/endo ratios found for the epoxidation of methylenenorbornane and norbornene, viz. 6.7 and 200, respectively.¹⁵

Conclusion

This study shows that hydroperoxidation of an olefin by singlet oxygen is well described as a typical electrophilic reaction, the rate of which is controlled by the HOMO of the active double bond. To a first approximation the rate of photooxygenation is inversely proportional to the ionization potential of the double bond. For a series of olefins, any deviations from the predicted rate can be ascribed to the operation of steric effects. Although the model was based on an activated complex leading to perepoxide, the use of an enetype transition state would entail similar electronic and steric arguments leading to the same conclusions.²⁴

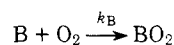
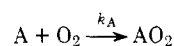
Experimental Section

General. The details of the chromatographic, spectroscopic, and photooxygenation procedures as well as the preparation of 2-methylnorbornene (1) and 2-methylenenorbornane (2) have already been described.³

Olefins. 1-Methylcyclopentene (7) was purchased from Fluka, Buchs. Methylenecyclopentane (8) was prepared by the Wittig reaction.¹⁶ **2-Methylenenorborn-5-ene (6).** The commercial product (purchased from Aldrich Chemical Co.) was rid of minor quantities (~5%) of its isomer 5 by GLC at 100 °C (5% FFAP on Chromosorb G). **2-Methylnorborna-2,5-diene (5).**²⁵ A solution of 18.4 g of freshly distilled and degassed norborna-2,5-diene (0.2 mol) in 50 mL of ether was added to 20.8 g of *N*-butyllithium (0.3–5 mol) in 250 mL of ether

at 0 °C.¹⁷ After stirring overnight, the violet-colored solution was added slowly under nitrogen to 60 g of methyl iodide (0.42 mol) in dry ether at –78 °C. The temperature was allowed to rise to 25 °C over 1 h and the solution was poured into ice-water. The organic layer was separated, washed, dried, and evaporated. Fractional distillation followed by preparative GLC (20% Apiezon on Chromosorb W) gave 3.8 g of 6 (18% yield): NMR (CCl₄) δ 1.85 (d, 3 H), 1.95 (m, 2 H), 3.2 (m, 1 H), 3.5 (m, 1 H), 6.1 (m, 1 H), 6.8 (m, 2 H); MS (*m/e*) 106 (M⁺, 79), 105 (38), 91 (100), 91 (100), 66 (53).

Photooxygenations. Determination of Relative Rates (Table II). The competition method, based on the disappearance of olefin, requires no calibration since only ratios of concentrations are measured.¹⁸ Moreover, the products are often unstable under GLC conditions, whereas the olefins are quite stable. A pair of olefins of roughly similar reactivity is dissolved in a standard solution of acetonitrile containing methylene blue. An inert standard is also added. Typically the mixture consists of ~1 mmol of each olefin and 0.5 mmol of benzene in 2 mL of solvent. The solution is then placed in the reaction vessel under oxygen, irradiated, and stirred to 0 °C.¹⁹ Small samples are taken at regular intervals and analyzed by GLC. Oxygen uptake is measured volumetrically. For a competition reaction between two olefins, A and B, the rate (*k*) can be expressed as follows:



If the oxygen concentration is constant then $k_A/k_B = \ln(A_0/A_t)/\ln(B_0/A_t)$ where A_0 and B_0 are the starting concentrations and A_t and B_t are the concentrations after time *t*.

Product Analyses. 2-Methylnorborna-2,5-diene (5). A solution of 0.48 g of 5 in 3 mL of acetonitrile (plus methylene blue) under an atmosphere of oxygen was irradiated at 0 °C until 95% reaction. Reduction was effected with sodium borohydride in methanol, giving 0.493 g of crude product which was purified by GLC (20% on Chromosorb W). The exo and endo allylic alcohols 9 and 10 were obtained in a ratio of 7.3:1 in a 72% yield. The distinction between 9 and 10 was made by NMR spectroscopy. Isomer 9 shows a W-type coupling between the anti C(7) and endo C(3) protons which is absent in isomer 10.²⁰ The exo and endo dispositions of the hydroxyl groups were further confirmed by using shift reagent.

Exo Isomer (9):²⁸ NMR (CDCl₃) δ 1.74 (d of t of d, 1 H), 1.9 (d of t of t, 1 H) [C(7) anti and C(7) syn, $^3J_{7a,1} = 1.5$ Hz, $^4J_{7a,3} = 1.5$ Hz, $^2J_{7a,7s} = 9.0$ Hz], 2.8 (m, 1 H), 3.12 (m, 1 H), 4.02 (m, 1 H), 4.98 (s, 1 H), 6.06 (d, 1 H); IR (film) 3500–3200, 3065, 2980, 1320, 1100, 1039, 890, 760, 720 cm⁻¹.

Endo Isomer (10): NMR (CDCl₃) δ 1.48 (d of t, 1 H), 1.72 (d of t of t, 1 H) [C(7) anti and C(7) syn, $^3J_{7a,1} = 1.8$ Hz, $^3J_{7s,1} = 1.5$ Hz, $^2J_{7a,7s} = 9.0$ Hz], 3.04 (m, 1 H), 3.16 (m, 1 H), 4.56 (m, 1 H), 5 and 5.06 (two s, 2 H), 6.14 and 6.40 (d of d, 2 H).

2-Methylenenorborn-5-ene (6). Olefin 6 (0.6 g, 5.6 mmol) in 3 mL of acetonitrile was irradiated for 2 h at 0 °C. After 80% absorption of 1 equiv of oxygen, the solvent was evaporated and the residue extracted with pentane. After further evaporation, column chromatography over silica gel (eluting with pentane/ether) effected removal of olefin 6 (15 mg). Subsequent thin-layer chromatography (silica gel, eluting with hexane/ether) gave *exo*-epoxide 12 (*R_f* 0.409, traces), *endo*-epoxide 13 (*R_f* 0.337, 15 mg), norbornenone 14 (*R_f* 0.313, traces), and lastly hydroperoxide 11 (*R_f* 0.297, 85 mg). After a 2% conversion of olefin 6 the percentage ratios of products were 0.2, 1.8, ~0.1, and 98%.

1-Hydroperoxymethylnorborna-2,5-diene (11): NMR (CDCl₃) δ 2.1 (s, 1 H), 3.6 (m, 2 H), 4.7 (d, 1 H), 6.75 (m, 1 H), 6.9 (m, 2 H), 8.25 (s, 1 H); IR (CCl₄) 3540 (m), 1675 (m), 1260 (w) cm⁻¹, MS (*m/e*) 138 (M⁺, 0.85), 120 (13), 91 (40), 66 (29), 18 (100). Treatment of 11 with triphenylphosphine in ether gave the corresponding alcohol. It was purified by chromatography over silica gel and identified by comparison with an authentic sample.²¹

Epoxides 12 and 13. These were identified with authentic samples.⁴

Norborn-5-en-2-one (14). This was identified by oxidizing 2-hydroxynorborn-5-ene.²²

Acknowledgments. We thank the Swiss National Science Foundation for support of this work (Grant No. 2.238.0.74). We thank J. C. Perlberger for carrying out the MINDO/3 calculations.

Registry No.—9, 56682-78-1; 10, 65102-12-7; 11, 65102-13-8.

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Oxidation of a Bicyclobutane-Bridged Diene with $^1\text{O}_2$ and O_3 . Wittig Reactions of the Corresponding Enone and Dione

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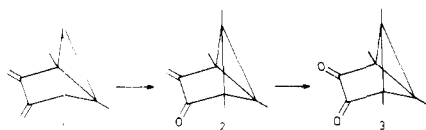
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Received June 13, 1977

Oxidation of 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane upon treatment with OsO_4 , $^1\text{O}_2$, and O_3 is reported. The corresponding bicyclobutane-bridged α,β -unsaturated ketone and α -diketone are used as starting materials in Wittig reactions, which in one case result in cyclopropane formation.

Oxidation of organic compounds constitutes a subject with numerous ramifications.¹⁻⁵ Hydrocarbon oxidation using transition-metal compounds, peracids, and peroxides together with photosensitized oxygenations and ozonization rank among the frequently employed methods in this area in which phase-transfer catalysis⁶ and crown ether chemistry⁷ are of increasing importance.

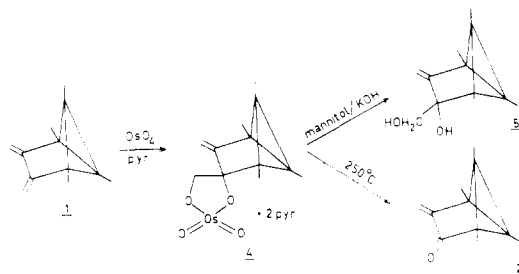
In view of the intriguing reactivity of tricyclic diene **1**,^{8,9} e.g., in Diels-Alder reactions, we aimed at synthesizing the corresponding enone **2** and diketone **3** from **1**. Two types of ke-



tone preparation involving carbon-carbon bond breaking, one-step and two-step cleavage reactions, are opportune. Apart from realization of the diene \rightarrow enone \rightarrow dione transformations, attention has to be paid to keep the bicyclobutane moiety intact. Generally speaking this leaves out the modes of oxidation which involve the use of acids and those in which the presence of certain transition metals is required. In the present paper the results of some oxidation reactions (e.g., O_3 , $^1\text{O}_2$) of compound **1** are described, together with those of the Wittig reactions of enone **2** and dione **3**.

Oxidation of 1. A. Osmium Tetroxide. The highly poi-

sonous osmium tetroxide can be employed to convert olefins to glycols or ketones, depending upon reaction conditions; the initially formed adducts in many cases are of sufficient stability to permit their isolation.^{10,11} Upon addition of osmium tetroxide at room temperature to diene **1** in ether containing pyridine (10:1), a brown precipitate was formed immediately. To this compound structure **4** is tentatively assigned. Sup-



porting data for the proposed structure were obtained by performing a reductive cleavage of **4** by mannitol in an alkaline solution, leading to glycol **5**, and a pyrolysis at 250 °C, affording α,β -unsaturated ketone **2**, which was trapped at -196 °C. However, this expensive route did not allow a large scale preparation of **2** and was abandoned for this reason.

B. Singlet Oxygen. Rearrangements of [2 + 4] adducts from singlet oxygen ($^1\text{O}_2$) and conjugated dienes¹² to α,β -unsaturated [2 + 2] adducts are known in the literature.¹³⁻¹⁵