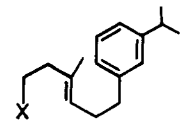
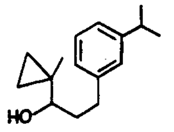


13 X = CH(COCH$_3$)COOCH$_3$
15 X = Br



14

boxaldehyde led to the cyclopropylcarbinol **14**, which was converted[13] into homoallylic bromide **15**. Alkylation of methyl acetoacetate with **15** gave **13**, which, on treatment with $SnCl_4/CH_2Cl_2$ at room temperature was transformed into the methyl ester of the racemic form of β,γ-unsaturated acid **11**,[14] an intermediate in the lactone **2** synthesis described above. As far as we are aware, this polyene cyclization represents the first case in which a β-keto ester unit acts as the initiator.[15,16]

Acknowledgments. The authors are grateful to the American Cancer Society for grant support (CH-48) and to R. G. Hoffmann of the Resins Division of the Organic Department, Hercules Inc., for a generous gift of pine rosin.

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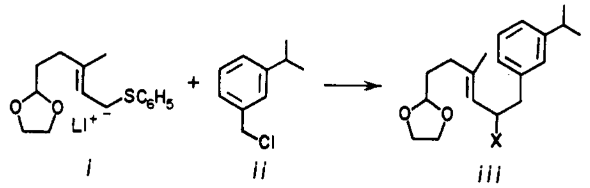
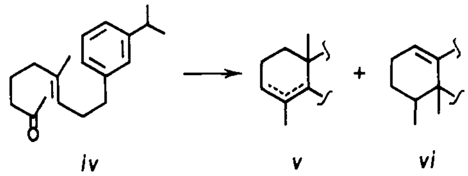
(2) As indicated by the base-induced conversion of **2** into the cis isomer (unpublished observation by Mr. J. Demers in this laboratory) as well as the exclusive formation of cis hydroxyamide by lactone ring opening of **2**.

(3) In this approach, thioether anion i was alkylated with benzyl halide ii,[4] yielding sulfide iii (X = SC_6H_5), which was reductively desulfurized with Ca/NH$_3$ to iii (X = H). Conversion of the latter into aldehyde was followed by treatment with $(C_6H_5)_3PC(OMe)CH_3$,[5] giving after hydrolysis ketone iv. Cyclization was carried out with $SnCl_4$ in methylene chloride, providing (50%) isomeric olefins in the ratio **3**:v:vi = 1:5:3.





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(14) Congeners have been tentatively identified as the ($\Delta^{4(5)}$ ester and the 3-carbomethoxyl counterpart of structure vi.[3]

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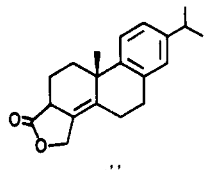


vii

(17) NSF Fellow, 1975-1978.

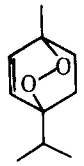
E. E. van Tamelen,* E. G. Taylor[17]
T. M. Leiden, A. F. Kreft III
Department of Chemistry, Stanford University
Stanford, California 94305

Received March 19, 1979

Organic Photochemistry with 6.7-eV Photons: Ascaridole[1]

Sir:

The ultraviolet absorption spectrum of ascaridole (**1**)[2] has not only a long, low-intensity absorption extending to 360 nm



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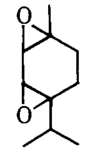

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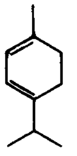

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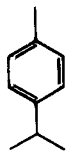

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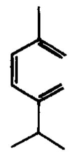
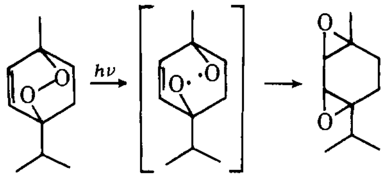


5

as in other peroxides,[3] but also a maximum at 233 nm (ϵ 166). It has been conjectured[2] that this "presumably implies interaction of the oxygen lone pairs with the double bond, perhaps in the antibonding orbital". The irradiation of this compound at 185 nm was of interest since such photon energy (6.7 eV) would correspond to the $\pi \rightarrow \pi^*$ absorption of the olefinic group. Studies on photochemistry of bichromophoric systems in the far-ultraviolet are few. Such studies would serve to answer the question if intramolecular coupling between chromophores in the excited states can be observed in the lifetimes of the excited states which tend to be quite short in the far-ultraviolet region.

In an earlier study of the photochemistry of ascaridole with light of wavelength >300 nm,[2] it was found that the only product was isoascaridole (**2**) which was formed in high yield. The reaction **1** → **2** was slow on direct irradiation, but was speeded up significantly when triplet sensitizers were used. The primary reaction (eq 1) was suggested[2] to involve cleavage to



(1)

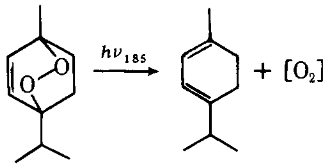
the diradical **6**, a process that would be consistent with the photochemistry of peroxides at long wavelengths.[3]

Photolysis of ascaridole of 185 nm in hydrocarbon solution[4] gave isoascaridole (**2**), α-terpinene (**3**), the triene **5**, a trace of *p*-cymene (**4**), and oxidation products derived from the solvent which were cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone when the solvent was cyclohexane. At low conversions (<15%), the mass balance as shown by the following equalities was satisfactory to ±5%:

$$\alpha\text{-terpinene} + \text{triene } \mathbf{5} \equiv \text{cyclohexyl hydroperoxide}^{5} + \text{cyclohexanol} + \text{cyclohexanone}$$

$$\Delta\ \text{ascaridole} \equiv \text{isoascaridole} + \alpha\text{-terpinene} + \text{triene } \mathbf{5}$$

Evidently, at 185 nm, the photolysis of ascaridole leads not only to isoascaridole as at longer wavelengths[2] but also to a retro-Diels–Alder reaction as shown in eq 2.



(2)

1 **3**

The triene **5** is believed to be predominantly a secondary isomerization product derived from α-terpinene by the well-known photochemical transformation of 1,3-cyclohexadienes. This was confirmed in a separate experiment in which a solution of α-terpinene alone was irradiated at 254 nm when **5** was observed to be formed. The ratio of process 2 to process 1 at 185 nm was 1:2.

The intriguing aspect of reaction 2 is that (according to gas chromography) not a trace of the oxygen that should be released was observed to accumulate in the solution. Further, the oxidation products of the solvents that are reported above closely resemble those from the direct irradiation at 185 nm of oxygen dissolved in the same solvents.[6] In view of the 40-fold weaker absorption of oxygen at 185 nm compared with the absorption of ascaridole at the same wavelength, the possibility that the oxygen released in reaction 2 undergoes secondary photolysis can be discounted. The conclusion that is inevitable is that the retro-Diels–Alder reaction (2) gives oxygen in an electronically excited state which invariably reacts with the solvent. The parallel between the product compositions in this and the O_2–hydrocarbon system suggests that this state may be $O_2(^3\Sigma_u^-)$ but a closer examination indicates another possibility as well.

Recently, Turro, Chow, and Rigaudy[7] found that the pyrolysis of certain 1,4-anthracene endoperoxides gave in nearly quantitative yield the aromatic hydrocarbon and oxygen ($^1\Delta$). The process

$$\text{anthracene endoperoxide} \xrightarrow{\Delta} \text{anthracene} + O_2(^1\Delta) \quad (3)$$

would evidently conserve spin, whereas the process

$$\text{anthracene endoperoxide} \xrightarrow{\Delta} \text{anthracene} + O_2(^3\Sigma_g^-) \quad (4)$$

would not. The conservation of spin may or may not be a strong consideration since reaction 4 competed successfully against 3 in 9,10-anthracene endoperoxides but not in 1,4-anthracene endoperoxides.

In applying these considerations to ascaridole, it can be seen that

$$\text{ascaridole} \xrightarrow{h\nu_{185}} \alpha\text{-terpinene (ground singlet)} + O_2(^3\Sigma_u^-) \quad (5)$$

is energetically possible[8] but does not conserve spin while

$$\text{ascaridole} \xrightarrow{h\nu_{185}} \alpha\text{-terpinene (triplet)} + O_2(^3\Sigma_u^+) \quad (6)$$

would conserve spin and energy. The $^3\Sigma_u^+$ state of oxygen is 35 713 cm^{-1} (102.1 kcal/mol) above the ground state so that ~53 kcal/mol will be available to excite the α-terpinene to its triplet state. It is at present not possible to choose between these alternatives because (i) the similarity in the composition of the oxidation products from the solvent in the ascaridole–cyclohexane system to the O_2–cyclohexane system may mean that either reaction 5 is the preferred made of photodecomposition of ascaridole or, in the O_2–cyclohexane system, the active species is not $O_2(^3\Sigma_u^-)$ but $O_2(^3\Sigma_u^+)$; (ii) the fate of the α-terpinene (other than deactivation) should give information on whether it is formed in its ground state or its triplet state. Unfortunately, the host of products that are formed in the photolysis of ascaridole makes this task difficult.

We are currently undertaking the flash photolysis of ascaridole in the vapor phase and expect to determine unequivocally the character of the oxygen as it is formed in reaction 2.

Photolysis of ascaridole offers a second route to the production of an upper excited state of oxygen in the condensed phase.

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(10) NIH Career Development Awardee (1975–1980).

R. Srinivasan,* Karen H. Brown, Jose A. Ors, Lloyd S. White
IBM Thomas J. Watson Research Center
Yorktown Heights, New York 10598

Waldemar Adam[10]
Department of Chemistry, University of Puerto Rico
Rio Piedras, Puerto Rico 00931

Received July 25, 1979

Crystal Structure and Dynamic Behavior of $Ir_4(CO)_{10}$(diars). A New Pathway for Carbonyl Scrambling in $M_4(CO)_{12}$ Derivatives

Sir:

The solid-state structures established for $Rh_4(CO)_{12}$ (C_{3v})[1] and $Ir_4(CO)_{12}$ (T_d)[2] formed a natural basis for the mechanism ($C_{3v} \leftrightarrow T_d$) proposed by Cotton et al. for the carbonyl scrambling in $Rh_4(CO)_{12}$.[3] Specific evidence for interconversion of T_d- and C_{3v}-like forms recently has been reported for the derivatives $Ir_4(CO)_{11}(PPh_2Me)$ (C_{3v})[4] and $Ir_4(CO)_{11}[CN(t\text{-Bu})]$ (T_d).[5] Nevertheless, ^{13}C NMR data reported for C_{3v}-like $RhCo_3(CO)_{12}$ provide evidence for a lowest energy scrambling process that is incompatible with $C_{3v} \leftrightarrow T_d$ interconversions.[6] Rationales for this apparent anomaly have been advanced in two recent discussions of carbonyl scrambling in $M_4(CO)_{12}$ derivatives.[7,8] We report herein a second anomalous case in the compound $Ir_4(CO)_{10}$(diars) (diars = 1,2-bis(dimethylarsino)benzene), which displays dynamic behavior that in part requires a new mechanistic proposal.

0002-7863/79/1501-7425$01.00/0