two isomeric desmethoxy dihydrocorynantheine alcohols (**20** and **21**, Scheme III) in addition to dihydrocorynantheine alcohol (**22**), the desired reduction product.[10]

We intended to study the behavior of **1**, the cyclic analogue of **19**, under similar conditions. But in this case nothing unusual, excepting normal ester group reduction, happened, producing ajmalicinol (**23**). Even prolonged (72 h) refluxing with LAH in THF caused no unusual change in **1**.

Experimental Section

General Methods. Melting points were recorded in a Kofler block and are uncorrected. Preparative TLC was done with silica gel (Gouri Chemicals, Calcutta). The UV spectra were recorded in a Varian 634 spectrophotometer, IR spectra in a Beckman IR-20 spectrometer, and 80-MHz ^{1}H NMR and ^{13}C NMR spectra in a Varian CFT-20 spectrometer, Me_4Si being used as an internal standard. All reactions were carried out under a completely dry, oxygen-free nitrogen blanket.

Preparation of Ajmalicine Hemiacetal (2). Ajmalicine 1, (100 mg) was refluxed with 15 mL of 5% sulfuric acid. From the reaction mixture was separated **2** by prparative TLC, and it was crystallized from a benzene–ethyl acetate mixture: 40 mg; UV (EtOH) 226, 283, 289 nm; IR (KBr) ν_{NH} 3380 cm^{-1}; $_1$H NMR ($CDCl_3$) δ 7.6 (s, NH), 7.4–6.8 (m, aromatic protons), 5.05 (d, C-17 H), 4.15 (m, C-19 H), 3.75 (s, ester methyl), 1.23 (d, J = 6 Hz, C-19 methyl).

Preparation of Ajmalicine Acetal (6). Compound 1 (100 mg) was refluxed with 5% methanolic sulfuric acid for 45 min. **6** was isolated by preparative TLC and purified by crystallization from a benzene–methylene ch loride mixture: 35 mg; UV (EtOH) 225, 282, 290 nm, maximum at 249 nm; IR (KBr) ν_{NH} 3400, ν_{CO} 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.95 (s, NH), 7.5–7.0 (m, aromatic), 4.65 (d, C-17 H), 4.13 (m, C-19 H), 3.71 (s, ester methyl), 3.34 (s, methoxyl), 1.12 (d, J = 6 Hz, C-19 methyl).

Preparation of Ajmalicial (12 and 14). Compound 1 (100 mg) was refluxed with 3 N hydrochloric acid at 160 °C for 2 h. Ajmalicial was the sole product, and it was purified by crystallization. For **12**: IR (KBr) $\nu_{NH/OH}$ 3280 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 10.64 (s, NH), 7.3–6.8 (m, aromatic), 6.02 (d, J = 6.5 Hz, C-17 hydroxyl), 4.86 (t, C-17 H), 4.0 (m, C-19 H), 1.12 (d, J = 6.2 Hz, C-19 methyl). For **14**: IR (KBr) $\nu_{NH/OH}$ 3390 cm^{-1}.

Preparation of Ajmalicinol (23). To an ice-cold solution of 1.0 g of LAH in 50 mL of dry ether was added a solution of 100 mg of **1** in 75 mL of dry ether slowly and with stirring, which was continued for 24 h at 28–30 °C. Excess LAH was the decomposed with ice chips, and the organic portion was extracted from the mixture with ether. The combined ethereal layer was washed, dried and concentrated to afford a gummy solid. Crystallization from a benzene–chloroform mixture (4:1) furnished 60 mg of light yellow granular **23**: $C_{20}H_{24}N_2O_2$; mass spectrum, m/e 324.1860 (M$^+$); mp 236–238 °C; UV (EtOH) 226, 283, 290 nm; IR (KBr) ν_{OH} 3520, ν_{NH} 3360, $\nu_{C=C}$ 1655 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.4–6.5 (aromatic), 6.17 (s, C-17 H), 4.15 (m, C-19 H), 1.05 (d, J = 6.5 Hz, C-19 CH_3).

Acknowledgment. Sincere thanks are accorded to Mr. Somnath Ghosh and Dr. A. Banerji of our department for helpful suggestions and to Mr. D. J. Roy for helping in the experimental work. We are also thankful to Dr. B. C. Das (Institut de Chimie des Substances Naturelles, France), Professor F. Bohlmann (Institut für Organisch Chemie der Technischen Universität, West Berlin), and Professor M. Hesse (Organisch-Chemisches Institute, University of Zürich, Zürich) for mass spectral analyses. Finally, financial assistance from CSIR (India) to S.B. is gratefully acknowledged.

Registry No. 1, 483-04-5; 2, 81737-76-0; 6, 63569-19-7; 7, 63569-20-0; 12, 81737-77-1; 12 acetyl, 81671-29-6; 14, 81671-27-4; 16, 81671-28-5; 23, 60490-96-2.

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[10] Karrer, P.; Schwyzer, R.; Flam, A. *Helv. Chim. Acta* **1952**, *35*, 851.

Laser-Induced Cycloadditions: The Carvone Photoisomerization[†]

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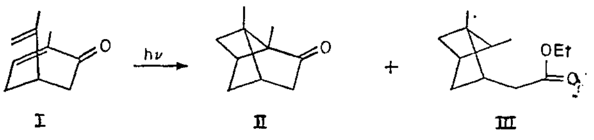
Received August 18, 1981

Laser flash photolysis of carvone yields triplet carvone. The lifetime is 75 ns in ethanol and 47 ns in cyclohexane. The photoisomerization reaction induced by UV pulsed lasers in the 350-nm range (XeF, 350 nm; YAG (third harmonic), 353 nm) gives carvone-camphor and trace amounts of 1-*exo*,5-dimethyl-*syn*-2-[(ethoxycarbonyl)-methyl]bicyclo[2.1.1]hexane. Photolysis with a CW laser, in the same wavelength region (Kr ion, 350.7- and 356.5-nm lines), results in a different product distribution. The differences are explained tentatively in terms of multiphotonic UV photolysis.

Introduction

The intramolecular photocycloaddition of carvone (I) to give carvone-camphor (II) was among the very first photochemical reactions studied and through the years the yield of II has been improved considerably from about 9% to 35%, by a careful choice of experimental conditions.[1–4]



Recently Zandomenghi[5] et al. investigated the photolysis using a Kr ion laser (350.7- and 356.5-nm lines) and reported a photoisomerization yield of about 88%. This was reported also to minimize the ring opening of II to the corresponding 1-*exo*,5-dimethyl-*syn*-2-[(ethoxycarbonyl)-methyl]bicyclo[2.1.1]hexane (III) and the concomitant

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[†] Issued as NRCC 20357.

[1] G. Ciamician and P. Silber, *Chem. Ber.*, **41**, 1928 (1908).

[2] G. Büchi and J. M. Goldman, *J. Am. Chem. Soc.*, **79**, 4741 (1957).

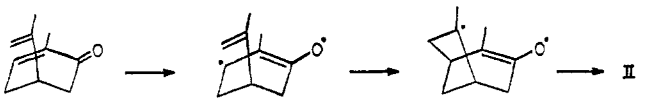
[3] (a) J. Meinwald and R. A. Schneider, *J. Am. Chem. Soc.*, **87**, 521 (1965); (b) J. Meinwald, R. A. Schneider, and A. F. Thomas, *ibid.*, **89**, 70 (1967).

[4] T. Gibson and W. F. Erman, *J. Org. Chem.*, **31**, 3028 (1966).

[5] M. Zandomenghi, M. Cavalla, L. Moi, and F. Pietra, *Tetrahedron Lett.*, **21**, 213 (1980).

formation of polymeric materials. We have investigated this system using radiation from high-power pulsed lasers [XeF excimer (350 nm) and third harmonic YAG (353 nm)] and extended the wavelength range with the XeCl laser (308 nm).

Further, in order to more fully establish the photochemical mechanism, we have made a systematic study of the photophysical kinetics of the carvone system using laser flash photolysis techniques. This was necessary because although there has been a good deal of speculation, little firm experimental data on the behavior of the photoexcited states in the system exists in the literature. Among the speculations is that of Büchi and Goldman[2] who proposed formation of a biradical intermediate in the production of II from I.



Zandomenghi et al.[5] expanded this posit by suggesting that the (first) excited state leading to the photoproducts is a triplet (of unspecified configuration). We have now defined the multiplicity and the configuration of the reactive excited state and measured its lifetime and temperature dependence.

Experimental Section

The three compounds were separated on a 12 ft × $^{1}/_{8}$ in. 12% Carbowax 20M column at 150 °C. The retention times of I, II, and III were 26.1, 13.1, and 20 min, respectively. Blank runs were conducted routinely and the corrections made accordingly. The reported results are estimated to be reliable to ±10%. A krypton ion laser (Coherent Model 3000) was used for output of 350.7- and 356.5-nm lines; XeF and XeCl outputs were obtained with a Lumonics Model 860 excimer laser; and the 3rd harmonic YAG output was obtained from a Molectron Model 34Y amplifier–oscillator system. Pulse energies were measured with a Scientech Model 36001 power meter.

Samples for laser irradiation were prepared by standard vacuum line techniques and contained in fluorescence or UV cells of either 10- or 2-mm pathlength. The carvone was obtained from Aldrich and purified by VPC on a 6 ft × $^{3}/_{8}$ in. Carbowax 20M 1.5% on Chromosorb WHP column at 150 °C. In the quantitative calculation of the percentages, each area was multiplied by a correction factor obtained from VPC analysis of stock solutions of carvone, carvone-camphor, and the ethyl ester III.

The laser flash photolysis experimental procedure has been described elsewhere.[6] Samples were excited with the pulses (337.1 nm, ca. 8 ns, ca. 10 mJ) from a nitrogen laser. All the experiments were carried out under oxygen-free conditions.

Results and Discussion

Photolysis with Kr Ion Laser (350.7- and 356.5-nm Lines), XeF Laser (350 nm), and Third Harmonic YAG (353 nm). The progress of the photoisomerization of a 1.1×10^{-3} M ethanolic solution of either *l*- or *d*-carvone, was followed by gas chromatography. The data from XeF and Kr ion laser photolysis are compared in Figure 1 and summarized for all sources used in Table I. One notable difference is in the yield of product III. The two pulsed sources XeF and third harmonic YAG give almost negligible yields of the ring-opening product III, whereas with the Kr ion laser, at essentially the same wavelength and similar conversions of starting material, the yield of III represents well over 10% of the total yield of photoproducts.

During the irradiation with the Kr ion laser some local overheating of the solution occurred because of the small beam size. This was overcome by expanding the beam with a quartz cylindrical lens without affecting the ratio II/III.

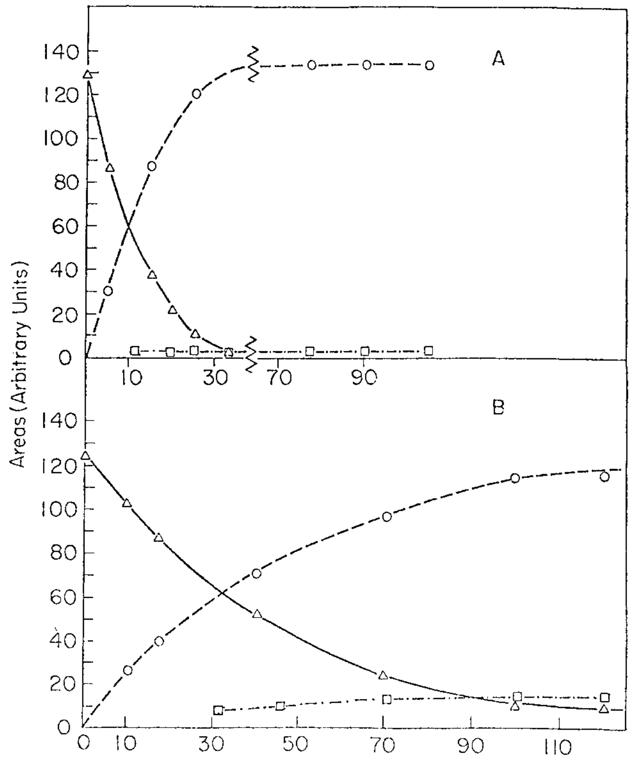
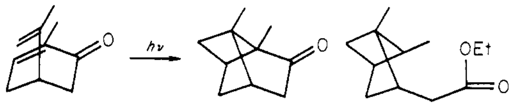


Figure 1. Product distribution upon photolysis of (△) 1.1×10^{-3} M carvone in ethanol with (A) XeF laser and 1-*exo*,5-dimethyl-*syn*-2-[(ethoxycarbonyl)methyl]bicyclo[2.1.1]hexane. Kr ion laser operated at the same average power of ca. 1 W; (○) carvone-camphor; (□) 1-*exo*,5-dimethyl-*syn*-2-[(ethoxycarbonyl)methyl]bicyclo[2.1.1]hexane.

Table I. Percent Composition of the Reaction Mixture upon Photolysis of Carvone at Various Wavelengths



I II III

laser/wavelength, nm	II	III	I
XeF/350	94.4	2.1	3.5
YAG(×3)/353	96.1	2.3	1.6
Kr ion/350.7, 356.5	81.7	9.3	9.0
XeCl/308		98	2.0
I + sunlight	9		91

Photolysis with a XeCl Laser (308 nm). The photolysis of 5 mL of a 1.1×10^{-3} M solution of *l*-carvone in EtOH (96.6% Fluka puriss) for 750 s (10 Hz, 80 mJ/pulse) gives III in high yield ca. 97% and only traces of carvone and carvone-camphor were present in the reaction mixture. The gas chromatographic analysis of the reaction at different times (Figure 2) reveals an initial buildup of the photoisomer carvone-camphor, which is the photolyzed to 1-*exo*,5-dimethyl-*syn*-2-[(ethoxycarbonyl)methyl]bicyclo-[2.1.1]hexane.

Laser Flash Photolysis. Irradiation of *l*-carvone in 0.08 M in ethanol (Fluka) by a nitrogen laser (337 nm) leads to the transient spectrum shown in Figure 3. This transient can be quenched by conjugated dienes (e.g., 2,5-dimethyl-2,4-hexadiene) and by 1-methylnaphthalene; in the latter case, the quenching occurs concurrently with the generation of the characteristic spectrum of the triplet state of the acceptor.[7] On this basis, the spectrum in

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(6) J. C. Scaiano, *J. Am. Chem. Soc.*, **102**, 7767 (1980).

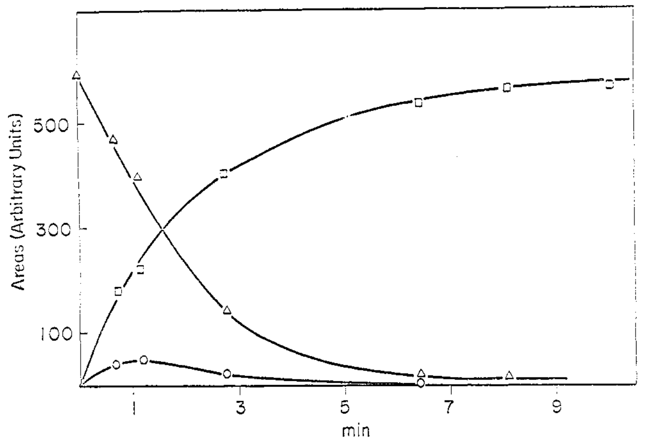

Figure 2. XeCl laser photolysis of 1.1×10^{-3} M carvone in ethanol: (△) carvone, (○) carvone camphor, (□) 1-*exo*,5-dimethyl-*syn*-2-[(ethoxycarbonyl)methyl]bicyclo[2.1.1]hexane.

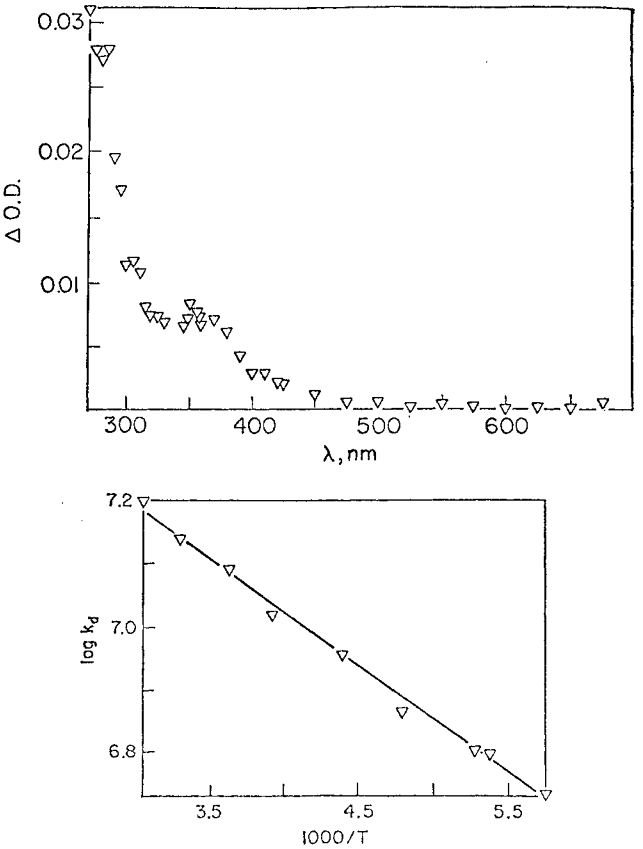

Figure 3. Top: absorption spectrum of the triplet carvone in ethanol. Bottom: temperature dependence for the rates of triplet decay between 186 and 328 K.

Figure 3 is assigned to the triplet state of carvone and bears significant resemblance to those reported by Bonneau[8] for other enones. The lifetime of the carvone triplet state is 75 ns at 26 °C and shows only a very small temperature dependence. Examination of the rates of triplet decay from 186 to 328 K leads to

$$-\log \tau_T = 7.70 - 780 \text{ cal mol}^{-1} (2.3RT)^{-1} \quad (1)$$

where τ_T is given in seconds.

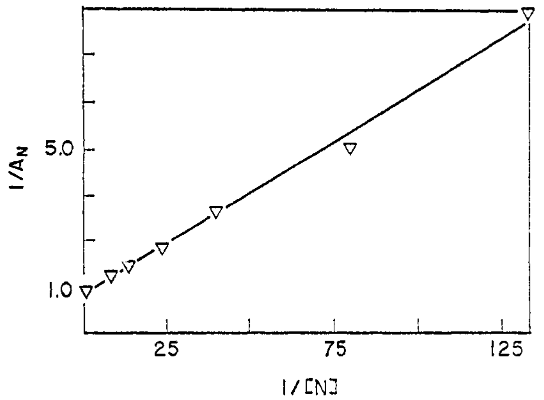

Figure 4. Stern–Volmer plot for the quenching of triplet carvone by 1-methylnaphthalene in ethanol at 299 K in ethanol.

As mentioned before, the addition of 1-methylnaphthalene leads to the formation of its triplet state which shows strong T–T absorption at 420 nm. The yield of triplet (ϕ_N) should follow a Stern–Volmer type of dependence:

$$1/\phi_N = 1 + 1/k_q\tau_N[N] \quad (2)$$

or in terms of the optical density at 420 nm:

$$1/A_N = \alpha + \alpha/k_q\tau_N[N] \quad (3)$$

where [N] is the concentration of 1-methylnaphthalene and α is a proportionality constant.

A plot according to eq 3 for carvone in ethanol is shown in Figure 4; from this and a similar plot for carvone in cyclohexane we obtained $k_q\tau_T$ values of 190 and 105 M^{-1} at 26 °C in ethanol and cyclohexane, respectively. Combination of the former with the triplet lifetime measured directly (vide supra) leads to $k_q = 2.5 \times 10^9$ M^{-1} s^{-1} in ethanol. Typical values for phenyl alkyl ketones, with triplet energy of around 73 kcal/mol, in solvents of similar viscosity are usually 10^{10} M^{-1} s^{-1}.[9] We take this as an indication that the triplet energy transfer for the carvone triplet to methylnaphthalene is only slightly exothermic, which in quantitative terms puts the triplet energy between 60 and 66 kcal/mol.

Ethanol and cyclohexane have similar viscosities at room temperature; it is therefore reasonable to assume that the same values of k_q will be applicable in both solvents. On this basis, it is possible to use the above value of 105 M^{-1} to estimate a triplet lifetime of 42 ns in cyclohexane.

The yields of 1-methylnaphthalene triplets can also be used to estimate the quantum yields of intersystem crossing if acetophenone (for which $\phi_{isc} = 1.0$) is used as actinometer. The details of this approach have been published elsewhere.[6] Experiments of this type give values for ϕ_{isc} of 0.86 and 0.77 in ethanol and cyclohexane, respectively.

The linearity of the quenching plots of Figure 4 suggests the involvement of only one triplet state from carvone; i.e., molecules with more than one triplet state are known to lead to curved plots.

We have also observed that the lifetime of the triplet 1-methylnaphthalene (produced by energy transfer from carvone) is dependent upon the concentration of carvone. In other terms, carvone behaves as both a sensitizer *and* a quencher at the same time. This effect is probably the result of reversible energy transfer so that the equilibrium concentration of triplet carvone, even if small, continues to decay with τ_T = 75 ns, thus providing a mechanism for

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(7) G. Porter and M. W. Windsor, *Proc. R. Soc. London, Ser. A.*, **245**, 238 (1958).

(8) R. Bonneau, *J. Am. Chem. Soc.*, **102**, 3816 (1980).

(9) P. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 1245 (1966).

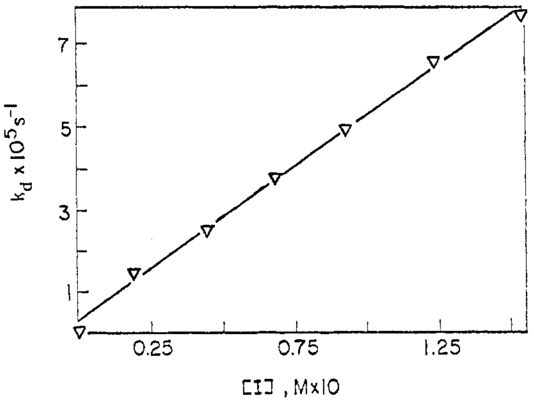


Figure 5. Decay of the triplet 1-methylnaphthalene as function of the carvone concentration at 25 °C for [N] = 0.072 M in ethanol.

triplet leakage.[9] Reactions 4 and 5 illustrate the mechanism proposed. Here I represents carvone. The first-order

$$^3N + I \overset{K_{eq}}{\rightleftarrows} N + {}^3I \quad (4)$$

$$^3I \rightarrow \text{decay} \quad (5)$$

decay of ^3N has been excluded from the mechanism because under our conditions, the lifetime of ^3N, in the absence of carvone quenching is much longer than those obtained in these experiments. If ^3N–^3I equilibration is achieved, then eq 6 adequately represents the apparent

$$d[^3N]/dt = K_{eq}[I][^3N]/\tau_T[N] \quad (6)$$

decay kinetics for the naphthalene triplet. The decay is therefore expected to follow first-order kinetics with a rate of decay, k_d, given by

$$k_d = K_{eq}[I]/\tau_T[N] \quad (7)$$

The experimental rates of decay do indeed follow first-order kinetics and the values of k_d depend linearly upon the concentration of carvone, as shown in Figure 5. The slope of the plot, k_{app}, equals 4.80×10^5 M^{-1} s^{-1} for [N] = 0.072 M in ethanol at 25 °C and is given by eq 8. From

$$k_{app} = K_{eq}/\tau_T[N] \quad (8)$$

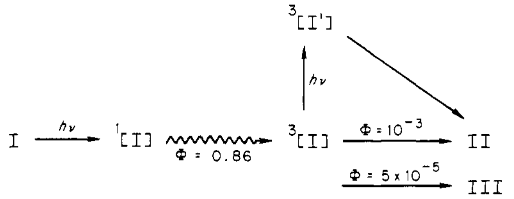
the data presented above we obtain $K_{eq} = 0.026$. If we assume that reaction 3 is isoentropic, we can estimate its enthalpy change as 2.2 kcal/mol; i.e., the triplet state of carvone lies 2.2 kcal/mol above that of 1-methylnaphthalene, which puts the triplet energy at 61.8 kcal/mol within the range of values estimated above.

The experiments described above, using eq 2 and 3, were carried out under conditions where τ_T(naphthalene) ≫ τ_T(carvone); thus, the equilibrium of eq 4 was displaced toward the left, and the concentration of ^3I was low enough that, at first approximation, it would not affect the measured yields of triplet 1-methylnaphthalene.

Pulsed vs. CW Laser Excitation. Earlier in this paper it was noted that the ring-opening product III is formed in barely detectable amounts on photolysis with either a XeF (350 nm) or a YAG laser (third harmonic, 353 nm), whereas we have confirmed that minor but significant ring-opening product is obtained in photolysis with CW Kr ion lasers. The photoisomerization reaction of carvone to carvone camphor, i.e., I → II, and the subsequent ring opening of II to III are characterized by rather low quantum yields: 1×10^{-3} and 8×10^{-5}, respectively.[5] The very small extinction coefficient of II at the photolyzing wavelength (350-nm range) accounts for the inefficiency of the ring-opening process resulting in the formation of the ethyl ester III compared to the high yields observed with XeCl laser radiation, at which wavelength III absorbs appreciably.

An inspection of Figure 1 and Table I reveals two interesting features. Firstly, the photolysis time necessary to achieve the same degree of conversion is about one-third shorter when a pulsed XeF laser is used instead of the CW Kr ion laser operating at the same average power (ca. 1 W). Secondly, the ratio II/III is considerably larger where a pulsed laser is used.

The results we obtain corroborate the suggestion by Zandomenghi[5] that III is a primary photoproduct. Although it is difficult to devise a detailed mechanism supporting the formation of III directly from I, the evidence so far obtained warrants a mechanism of the form:



where $^3I'$ is a second excited triplet of undefined structure. The suggestion of a two-photon route via an excited triplet state is put forward to explain the difference in behavior between pulsed and continuous laser photolysis in the 350-nm region. As shown in Figure 3, the transient triplet has a λ_{max} value of 350 nm. Furthermore, the high efficiency of the intersystem crossing process and the relatively long triplet lifetime lead to the triplet as the more likely to be absorbing a second photon. As part of the present series of experiments absorption measurements were carried out with the pulsed lasers at various intensities. Indications were that significantly more then one photon/molecule was absorbed; on average it was observed that 1.6 photons/molecule were absorbed with either the XeF or the YAG laser. The pulse durations of these lasers (10 ns for XeF, 5 ns for YAG) are relatively short compared to the triplet lifetime (75 ns), making it not unreasonable to interpret the >1 photon/molecule parameter as indicative of a two-photon process. It is necessary then that the upper triplet state must correlate with II more closely than with III as compared to the lower triplet state. Because of the very much lower photon flux obtained with the Kr ion laser, the two-photon possibility can be neglected and the formation of II and III directly from I must be the result of a partition mechanism of a "common" excited state, as the linearity of our Stern–Volmer plot (Figure 4) seems to suggest.

The mechanism for the photolysis at 308 nm might be different from the one posited for the 350-nm irradiation. Indeed, at the former wavelength the photoisomer II absorbs appreciably to undergo further photolysis to III and this latter compound does not need to be considered any more as a primary photoproduct.

In summary then, we have seen that by using lasers of appropriate wavelength, one can maximize the yields of either of the two products resulting from the photoisomerization of carvone.

In particular, at shorter wavelength (XeCl, 308 nm) III is the only product, whereas at longer wavelength, i.e., 350 nm, the photocycloaddition leading II to is the major reaction. Finally, the possibility of triggering multiphotonic processes with high intensity, pulsed lasers might offer the organic chemist alternative, convenient ways for selective chemistry.

In conclusion, it is worthwhile to briefly speculate on the likely mechanism of the carvone photoisomerization. The

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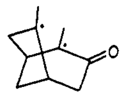
value of 61.8 kcal/mol which we find for the carvone triplet is, in all probability, indicative of a $\pi \rightarrow \pi^*$ configuration of the triplet state and is in excellent agreement with the value of 61 ± 1 kcal/mol estimated by Hammond[10] for the cyclohexenone ($\pi \rightarrow \pi^*$). Sensitization and quenching studies have shown that the photocycloaddition of cyclopentenones and cyclohexenones to olefins[10-12] involves triplet excited states. The initial interaction between the excited state and the olefins leads to the formation of a complex (exciplex) which then collapses to a 1,4 biradical[13,14] and ultimately gives the photoproduct. Attempts by laser flash photolysis to identify this biradical, i.e.



were unsuccessful.

Acknowledgment. Thanks are due to Dr. J. C. Scaiano for allowing us to use the laser flash photolysis facilities and for his helpful suggestions.

Registry No. *l*-I, 6485-40-1; *d*-I, 2244-16-8; II, 39196-52-6; III, 4638-90-8.

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Cytochalasin Support Studies.[1] The C_{14}–C_{19} Subunit of Cytochalasin C. Intramolecular 2 + 2 Photochemical Cycloaddition of Vinyl Sulfones[2]

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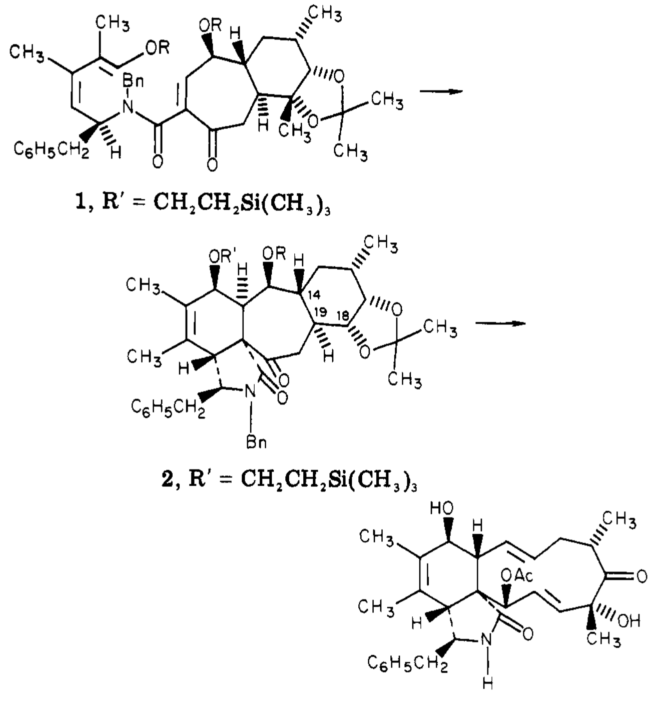
Received February 5, 1982

An intramolecular $2\pi + 2\pi$ photochemical cycloaddition between a six-membered ring vinyl sulfone and a five-membered ring vinylogous ester is described. The process occurs with moderate regiospecificity, the direction being controlled by a *cis*-acetonide moiety on the six-membered ring. Attempts to fragment the β-alkoxy sulfone adduct to trigger a DeMayo ring expansion were unsuccessful.

Introduction

One conceptual approach to the synthesis of the cytotoxic mold metabolite Cytochalasin C (**3**) involves the union of two strategies that we have established in simpler model systems,[4,5] namely, intramolecular Diels–Alder cyclization of the chiral (*Z*)-dienyl amide **1** to lactam **2**[6] followed by an enolate-promoted intraannular fragmentation to generate the eleven-membered ring diene moiety of Cytochalasin (**3**)[7] (Scheme I).

Scheme I



1, R' = $CH_2CH_2Si(CH_3)_3$

2, R' = $CH_2CH_2Si(CH_3)_3$

3

The plan for synthesis of the cyclization substrate **1** was based upon the union of the previously available chiral dienyl amine **4**[5] and the cycloheptenone carboxylic acid **5**. Synthesis of **5** was envisaged to arise (in several steps) via a DeMayo-type retroaldol strategy[8] with the polycyclic sulfone **34**. Construction of vinyl sulfone photochemical precursor **33** was projected to be possible from sulfinic acid elimination of either sulfoxide **18** or **19**, which in turn, could be prepared from olefin **13** (see Scheme II).

Results and Discussion

Conversion of 5-methyl-1,3-cyclohexanedione **6** to vinylogous ester **7** followed by lithium aluminum hydride reduction affords 5-methylcyclohex-2-en-1-one (**8**) in 78%

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[1] Cytochalasin Support Studies. 3. For paper 2 see S. G. Pyne, M. J. Hensel, S. R. Byrn, A. T. McKenzie, and P. L. Fuchs, *J. Am. Chem. Soc.*, **102**, 5962 (1980).

[2] Synthesis Via Vinyl Sulfones. 8. For paper 7 in this series see J. C. Saddler, and P. L. Fuchs, *J. Am. Chem. Soc.*, **103**, 2112 (1981).

[3] Postdoctoral Research Associate.

[4] D. A. Clark and P. L. Fuchs, *J. Am. Chem. Soc.*, **101**, 3567 (1979).

[5] S. G. Pyne, M. J. Hensel, and P. L. Fuchs, *J. Am. Chem. Soc.*, **104**, in press.

[6] For a successful realization of this goal see S. G. Pyne, D. C. Spellmeyer, S. Chen, and P. L. Fuchs, *J. Am. Chem. Soc.*, **104**, *0000* (1982).

[7] Although there are two diastereomeric trans-fused bicyclo[5.4.0] systems that could fragment to the *trans,trans*-undecadienone moiety of **3**, models suggest that the C-19 β-isomer **2** is the more desirable target molecule.

[8] (a) P. DeMayo, *Acc. Chem. Res.*, **4**, 41 (1970); (b) J. Kossanyi, *Pure Appl. Chem.*, **51**, 181 (1979); and references contained therein.

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