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Organic Photochemical Reactions. XXIV. Photocycloaddition of Propanal to 1,3-Cyclohexadiene[1]

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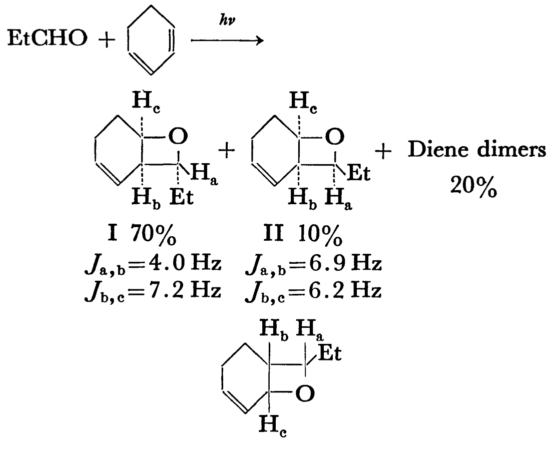
The photocycloaddition of propanal to 1,3-cyclohexadiene leads to oxetanes, as well as to the dimers of 1,3-cyclohexadiene. A mechanism of oxetane formation is proposed in which singlet excited propanal attacks a ground-state 1,3-cyclohexadiene to give a singlet complex with a charge-transfer character. The complex either decays to the ground-state reactants or reacts to give oxetanes. Quantum yield measurements and kinetic analysis show a rate constant of $4\times10^9\,M^{-1}\,s^{-1}$ for singlet complex formation from propanal and 1,3-cyclohexadiene in benzene. The quenching data of propanal fluorescence support such a mechanism.

The photocycloaddition of carbonyl compounds with olefins to form oxetanes is a topic of recent preparative and mechanistic interest.[3,4] Although a few cases are now known for which ketone singlets attack the olefins,[4c,4d,4e,4f] ketone triplets are generally thought to be the chemically active species in oxetane formation.[3] For electron-rich olefins the reaction is usually believed to involve an electrophilic attack[5] by the oxygen atom of the n,π^* state of the ketone on the olefin. For electron-deficient olefins, the reaction is considered to involve a nucleophilic attack by the electron-rich π^* orbital of the n,π^* singlet state of the ketone.[4d,4e,5] Recently, it has been suggested that an exciplex which leads to oxetane formation is formed between excited carbonyl compounds and olefins.[5,6] However, the reaction of excited carbonyl compounds with conjugated dienes has been little studied.[7] Conjugated dienes have frequently been used as quenchers of the triplet excited state of ketones because of their relatively low triplet energies.[8] However, in the case of benzophenone, the n,π^* triplet state can still undergo photoaddition to conjugated dienes to form oxetanes, in inefficient competition with triplet energy transfer.[7e]

Recently there has been interest in the interaction of acetone with conjugated dienes, studied both by the observation of the fluorescence quenching of singlet acetone[9] and by the isolation of oxetane products.[7b,7d,7f,7h,10] However, few attempts have been made to analyze the products[3g] and mechanism of photoaddition of alkanals such as propanal whose intersystem crossing rate constant seems to be as small as that of acetone.[11] In view of these facts, the photoreaction of propanal with 1,3-cyclohexadiene was investigated. We wish to report our results on the products and mechanism of the interaction of propanal with conjugated dienes;[12] it is interesting to compare our results with those of acetone.[7h]

Results and Discussion

Reaction Products. Irradiation of propanal in the presence of 1,3-cyclohexadiene resulted in the formation of oxetane I and II in good yield. Dimers of 1,3-cyclohexadiene were also formed as minor products. The products assigned the oxetane structures were 1: 1 adducts of propanal with the diene, and the IR spectra showed the absence of any carbonyl or hydroxyl group. Instead, each compound showed a strong band in the region 1000—900 cm^{-1}, which is the reported absorption region of the oxetane ring.[13] Oxetanes exhibited two signals near δ 4.7 and one signal near δ 3.0. The former absorptions were assigned to the ring protons α to the ring oxygen, while the higher field absorption was assigned to the ring hydrogen β to the ring oxygen. These are consistent with the reported absorption ranges.[3e,14] The stereochemical assignments for I and II were made on the basis of their vicinal H–H coupling constants in oxetanes. $J_{a,b}$ in the *cis*-isomer II is larger than that in the *trans*-isomer I and as large as $J_{b,c}$ in I and II. These are consistent with the reported observations.[15] The alternative orientation III of cycloaddition was ruled out by the fact that decoupling experiments showed the presence of the coupling between olefinic protons and H_b.



Mechanism. In these investigations, the irradiation of propanal with 1,3-cyclohexadiene was conducted in a Pyrex apparatus. Under these conditions, only propanal is excited to its n,π^* singlet state. The UV spectra showed no evidence for a ground-state complex of propanal with the diene. Formation of the diene dimers is thought to proceed *via* the attack of a triplet diene on another ground-state diene molecule.[16] Alkanals and alkanones are believed to have triplet energies of ≈80 kcal/mol,[17–19] and after efficient diffusion-controlled transfer[20] of triplet energy (E_T) to the diene (E_T=54 kcal/mol),[21] efficient formation of diene dimers is expected; therefore, the formation of oxetanes in good yield is mechanistically interesting.

The following routes are possible for oxetane formation: (i) triplet propanal attacks the diene directly to produce the oxetane; (ii) the triplet diene which is produced by energy transfer from triplet propanal attacks ground-state propanal;7c) or (iii) excited singlet propanal attacks the diene.

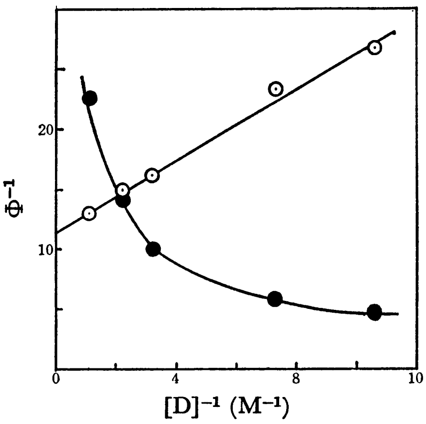


Fig. 1. Dependence of the reciprocal of the quantum yield for products formation on the reciprocal of 1,3-cyclohexadiene concentration; ○, oxetanes; ●, dimers. Slope=1.6 M, Intercept=11.6.

Figure 1 shows plots of the quantum yields for the formation of oxetanes and the diene dimers as a function of 1,3-cyclohexadiene concentration. The dimers decrease as the concentration of 1,3-cyclohexadiene increases. On the other hand, plots for oxetanes are linear up to high concentrations of 1,3-cyclohexadiene. This indicates that different precursors exist for the formation of oxetanes and dimers. It is well known that dimers are formed *via* diene triplets.16) Therefore, if oxetanes were formed by route (i) or (ii), dimers would have to increase with the concentration of 1,3-cyclohexadiene. This is incompatible with the results. Route (ii) is also ruled out by the fact that oxetanes are hardly obtained under conditions such as those under which triplet dienes are exclusively formed (phenanthrene-sensitized experiments). Therefore, route (iii) is thought to be the mechanism of this reaction. Furthermore, the following evidence indicates that oxetane formation results from the attack of singlet propanal on the diene: (a) the fluorescence of propanal is quenched by addition of 1,3-cyclohexadiene (Fig. 2); and (b) the yield of diene dimers decreases by *ca.* 20% in the presence of air, while that of oxetanes is unchanged. The quantum yield for oxetane formation is much lower than unity even at very high diene concentrations, implying that the reaction of propanal singlet with 1,3-cyclohexadiene is inefficient. The mechanism suggested in the following Scheme is conceivable. The observed inefficiency in formation of oxetanes can be accounted for by formation of an intermediate, C, which can collapse to oxetanes or to propanal and 1,3-cyclohexadiene.

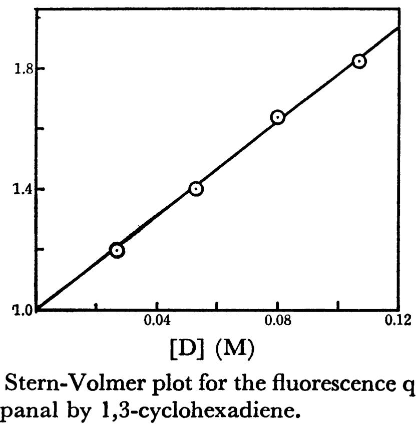


Fig. 2. Stern-Volmer plot for the fluorescence quenching of propanal by 1,3-cyclohexadiene.

$$
\begin{aligned}
\mathrm{P} &\xrightarrow{h\nu} {}^1\mathrm{P}\\
{}^1\mathrm{P} &\xrightarrow{k_1} \mathrm{P} + h\nu'\\
{}^1\mathrm{P} &\xrightarrow{k_2} \mathrm{P}\\
{}^1\mathrm{P} &\xrightarrow{k_3} {}^3\mathrm{P}\\
{}^1\mathrm{P} + \mathrm{D} &\xrightarrow{k_4} \mathrm{C}\\
\mathrm{C} &\xrightarrow{k_5} \mathrm{P} + \mathrm{D}\\
\mathrm{C} &\xrightarrow{k_6} \text{Oxetanes}\\
{}^3\mathrm{P} + \mathrm{D} &\xrightarrow{k_7} {}^3\mathrm{D} + \mathrm{P}\\
{}^3\mathrm{D} + \mathrm{D} &\xrightarrow{k_8} \text{Diene dimers}\\
{}^3\mathrm{D} &\xrightarrow{k_9} \mathrm{D}\\
{}^3\mathrm{P} &\xrightarrow{k_{10}} \mathrm{P}
\end{aligned}
$$

^{1}P: singlet propanal ^{3}P: triplet propanal
^{3}D: triplet 1,3-cyclohexadiene C: singlet complex

Steady-state treatment of the species ^{1}P, ^{3}P, ^{3}D, and C leads to the expressions

$$\frac{1}{\Phi_{\mathrm{ox}}} = \frac{k_5+k_6}{k_6} + \frac{(k_1+k_2+k_3)(k_5+k_6)}{k_4k_6}[\mathrm{D}]^{-1} \tag{1}$$

$$\Phi_{\mathrm{d}} = \frac{k_3k_7k_8[\mathrm{D}]^2}{(k_1+k_2+k_3+k_4[\mathrm{D}])(k_7[\mathrm{D}]+k_{10})(k_8[\mathrm{D}]+k_9)} \tag{2}$$

where Φ_{ox} and Φ_{d} are the quantum yields for the formation of oxetanes and dimers, respectively. The behavior predicted by Eq. 1 is observed experimentally, as shown in Fig. 1.

The rate of quenching of triplet propanal by 1,3-cyclohexadiene, k_7, is thought to be diffusion-controlled (in benzene, $5\times10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$).20) Therefore, if the rate of radiationless decay of the propanal triplet, k_{10}, is assumed to be $\approx 10^6\ \mathrm{s}^{-1}$,22) at concentrations of diene greater than 0.1 M, $k_{10} \ll k_7[\mathrm{D}]$ and Eq. 2 becomes Eq. 3.

$$\Phi_{\mathrm{d}} = \frac{k_3k_8[\mathrm{D}]}{(k_1+k_2+k_3+k_4[\mathrm{D}])(k_8[\mathrm{D}]+k_9)} \tag{3}$$

Rearranging Eq. 3 gives Eq. 4.

$$\frac{1}{\left(1+\frac{k_9}{k_8}[\mathrm{D}]^{-1}\right)\Phi_{\mathrm{d}}} = \frac{k_1+k_2+k_3}{k_3}\left(1+\frac{k_4}{k_1+k_2+k_3}[\mathrm{D}]\right) \tag{4}$$

Figure 3 is a plot of $\Phi_{\mathrm{d}}^{-1}(1+k_9/k_8[\mathrm{D}])^{-1}$ against [D], where k_9/k_8 is calculated from the data of Hammond and coworkers23) to be 0.03. Equation 4 explains the

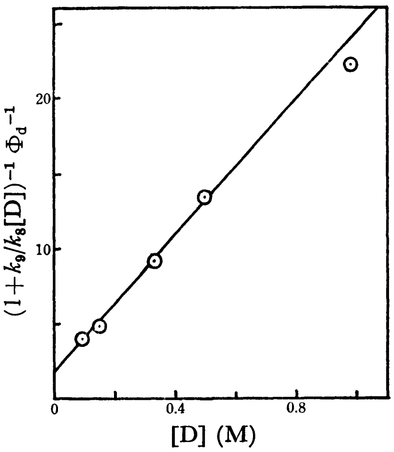


Fig. 3. Plot of $(1+k_9/k_8[D])^{-1}\Phi_d^{-1}$ against [D].

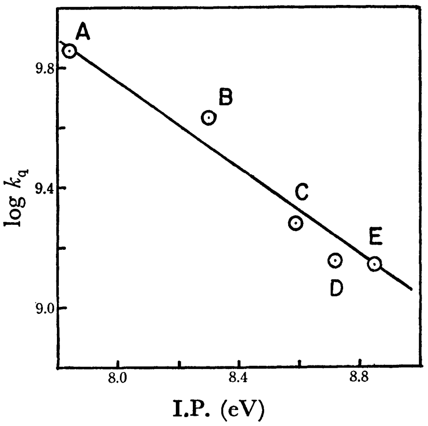


Fig. 4. Correlation of quenching rate constants for propanal with diene ionization potentials.

behavior of the dimerization of 1,3-cyclohexadiene qualitatively.

A Stern-Volmer treatment of the fluorescence quenching (Fig. 2) using Eq. 5 yields a slope of 7.8 M^{-1}.

$$\frac{F_0}{F} = 1 + \frac{k_4[D]}{k_1+k_2+k_3} \tag{5}$$

F_0: propanal fluorescence intensity in the absence of 1,3-cyclohexadiene

F: propanal fluorescence intensity in the presence of 1,3-cyclohexadiene

The slope and intercept of the Stern-Volmer analysis for oxetane formation with the diene (Fig. 1) show the following:

$$\frac{\text{intercept}}{\text{slope}} = \frac{k_4}{k_1+k_2+k_3} = 7.3\text{M}^{-1}$$

This is in good agreement with the value of $k_4/(k_1+k_2+k_3)$ obtained from the quenching of fluorescence of propanal by 1,3-cyclohexadiene, 7.8 M^{-1} (Eq. 5). These results indicate that the fluorescence quenching and oxetane formation by the diene proceed *via* the same intermediate and offer some experimental support to the kinetic Scheme proposed above.

The fluorescence of propanal was also quenched by other conjugated dienes (Table 1). The singlet excitation energy of 1,3-butadiene has been suggested to lie at 112 kcal/mol or somewhat higher[24] and that of 1,3-cyclohexadiene is unlikely to be very different. The lowest excited singlet level of propanal is expected to be a few kilocalories per mole below that of acetone (84 kcal/mol), since the absorption spectrum of propanal is red-shifted by ≈10 nm from that of acetone.[25] Therefore, such quenching is unlikely to proceed by physical energy transfer. It is noteworthy that the rate constants for quenching by 2,5-dimethyl-2,4-hexadiene and 1,3-cyclohexadiene are essentially equal to that for diffusion in the solvent, benzene. In Fig. 4 the function log k_q is plotted against ionization potentials of several 1,3-dienes. The linear behavior indicates that charge transfer interaction contributes to stabilization of this quenching process.[26] The efficient endothermic quenching and linear relationship between log k_q and ionization potentials suggest that the complex mentioned previously is an exciplex involving the interaction between the highest filled orbital of the conjugated diene and the half-vacant n-orbital of propanal.[5a] The simple Hückel MO calculations[27] suggest that the wave-function coefficient of the highest filled orbital of the conjugated diene is largest at the p-orbital of either end. Therefore, an attack by the non-bonding oxygen electron on either end of the diene generates a more stable exciplex. The stability of this exciplex seems to determine the regioselectivity of oxetane formation.

Table 1 shows that rate constants for quenching of propanal n,π* singlet state by dienes are 5—20 times greater than rate constants for quenching of acetone n,π* singlet state. These results are consistent with the data suggested by Dalton *et al.*[28] The greater reactivity of propanal n,π* singlet state toward dienes will probably be a steric effect, *i.e.*, that interaction of the highest filled orbital of conjugated dienes with the electrophilic oxygen *n* orbital in the plane of the carbonyl is less sterically hindered in aldehydes than in ketones, as

TABLE 1. DIENE IONIZATION POTENTIALS AND RATE CONSTANTS FOR FLUORESCENCE QUENCHING OF PROPANAL BY CONJUGATED DIENES

Diene	$k_q\tau$,M^{-1} [a]	k_q,M^{-1} s^{-1} [b]	I.P.,[c] eV
2,5-Dimethyl-2,4-hexadiene (A)	13 (2.07)	7.2×10^9	7.84
1,3-Cyclohexadiene (B)	7.8(1.45)	4.3×10^9	8.30
1,3-Pentadiene (C)	3.5(0.17)	1.9×10^9	8.59
2,3-Dimethyl-1,3-butadiene (D)	2.6(0.19)	1.4×10^9	8.72
Isoprene (E)	2.5(0.13)	1.4×10^9	8.85

a) $k_q=k_4$: quenching rate constants. The values in parentheses are those for acetone.[7h,9b]
b) Calculated from the data of Turro *et al.*, Ref. 9c. τ (the lifetime of singlet propanal) is estimated to be 1.8 ns. c) See Ref. 26.

suggested by Dalton *et al.*[11b]

Experimental

General. IR spectra were obtained on a Hitachi EPI-S2 spectrophotometer. UV spectra were obtained on a Hitachi 124 spectrophotometer. Fluorescence spectra were obtained on a Hitachi MPF-2A spectrofluorometer. NMR spectra were taken on a Hitachi Perkin-Elmer R-20 spectrometer. VPC were performed on a Shimadzu GC-3AF. A 2 m 25% PEG 6000 on a Chromosorb W column was used for analysis of the products.

Materials. Benzene was treated with concentrated sulfuric acid, washed with water, and finally purified by distillation over sodium. 1,3-Cyclohexadiene was prepared as described by Marvel and Hartzell.[29] 2,3-Dimethyl-1,3-butadiene was prepared by the method of Allen and Bell.[30] Propanal, 1,3-pentadiene, isoprene, and 2,5-dimethyl-2,4-hexadiene were obtained commercially, and were purified by distillation before use.

Irradiation of Propanal and 1,3-Cyclohexadiene. In a Pyrex vessel, a mixture of propanal (14.5 g, 0.25 mol) and 1,3-cyclohexadiene (20 g, 0.25 mol) was irradiated for 55 h with a 350 W high-pressure mercury lamp. After removal of the reactants, the remaining liquid was distilled under reduced pressure to give a liquid (5.9 g, bp 73—105 °C/18 mmHg), leaving a viscous liquid (1 g). VPC (PEG 6000, 130 °C) of the distillate showed oxetane I (70%), II (10%), and 1,3-cyclohexadiene dimers (20%). 1,3-Cyclohexadiene dimers were identified by a comparison of their VPC retention times (PEG 6000 and DNP) with those of authentic samples.[16] Oxetane I and II were isolated by preparative VPC on a 2 m 25% PEG 6000 column at 125 °C.

Oxetane I was collected as a colorless oil: bp 70—71 °C/18 mmHg; IR 1650 (C=C) and 982 cm^{-1} (oxetane ring); NMR (CCl_4) δ 0.90 (t, J=6.5 Hz, 3H, methyl), 1,1—2.5 (m, 6H, methylene), 2.76 (*ca.* q, 1H, H_b), 3.89 (td, J=4.0 and 6.0 Hz, 1H, H_a), 4.88 (dt, J=3.0 and 7.2 Hz, 1H, H_c), and 5.83 (m, 2H, olefinic). Found: C, 78.23; H, 10.40%; mol wt, (cryoscopic in benzene), 144. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21%; mol wt, 138.

Oxetane II was collected as a colorless oil: IR 1650 (C=C) and 983 cm^{-1} (oxetane ring); NMR (CCl_4) δ 0.73 (t, J=7.1 Hz, 3H, methyl), 1.0—2.5 (m, 6H, methylene), 3.10 (q, J=6 Hz, 1H, H_b), 4.63 (q, J=6.9 Hz, 1H, H_a), 4.90 (dt, J=2.5 and 6.3 Hz, 1H, H_c), and 5.83 (m, 2H, olefinic). Found: C, 78.00; H, 10.29%. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21%.

Quantum Yields. Benzene solutions (4 ml) containing 0.11 M propanal and 0.1—1 M 1,3-cyclohexadiene were degassed and sealed in 10 ml o.d. quartz tubes which had been attached to Pyrex tubes *via* graded seals. The sample tubes were then irradiated on a merry-go-round apparatus at room temperature, using a 350 W high pressure mercury lamp and a filter solution with a path length of about 1 cm containing 5 g potassium hydrogen phthalate made up to 1 l with distilled water (>310 nm). Photolysis was carried out to 10% or less conversion (irradiation time, 30 min); the conversion was linear out to 80 min. Actinometers (propanal–2-methyl-2-butene system)[4b] were photolyzed simultaneously. The solutions were analyzed on VPC (PEG 6000, 125 °C), using tetralin as the internal standard.

Sensitization with Phenanthrene. A benzene solution containing 0.12 M propanal, 0.13 M 1,3-cyclohexadiene, and 0.02 M phenanthrene was degassed, sealed, and irradiated for 20 min through a filter solution containing 15 g naphthalene made up to 1 l with hexane (>320 nm). The formation of oxetanes was only <1% of diene dimers, according to VPC, though it was expected to be 20% of diene dimers at such a diene concentration. The formation of a small amount of oxetanes was considered to be due to the directly excited propanal.

Fluorescence Quenching. A propanal solution, 0.2 M, was prepared in benzene. A known volume of the propanal solution was pipetted into a quartz fluorescence cell and the fluorescence was observed using an excitation wavelength of 320 nm. Aliquots of dienes were added to the solution by means of a micro syringe while monitoring the decrease in fluorescence intensity at 420 nm.

Quenching with Oxygen. Two samples were prepared. Each contained 4.0 ml of a benzene solution of 0.13 M propanal and 0.052 M 1,3-cyclohexadiene. One was degassed and sealed. Both samples were irradiated for 45 min with a 350 W high pressure mercury lamp through a potassium hydrogen phthalate cut-off filter (>310 nm). The yield of diene dimers in the non-degassed sample was less than that in the degassed sample by *ca.* 20%, but that of oxetanes was unchanged in both samples, according to VPC (PEG 6000, 125 °C).

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