The Photoaddition of Propionaldehyde to Cyclohexa-1,3-diene. Oxetan Formation by a Singlet Mechanism

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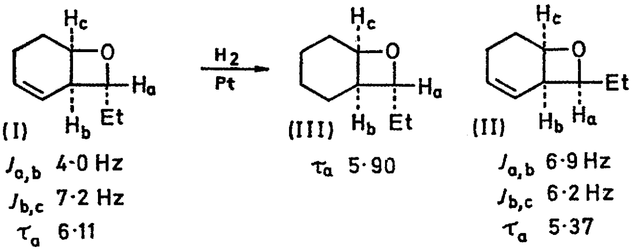
Summary Excited singlet propionaldehyde attacks conjugated dienes to give oxetans.

CONJUGATED dienes are widely used as triplet quenchers on account of their relatively low triplet energies. In our recent study of the photocycloaddition reactions between propionaldehyde and olefins, we found that the photocycloaddition of propionaldehyde to the conjugated diene used as a triplet quencher occurs easily. We investigated the photocycloaddition of propionaldehyde to various conjugated dienes, and confirmed that this reaction proceeded *via* an excited singlet state of propionaldehyde (possibly *via* singlet complexes).



Irradiation of propionaldehyde in the presence of cyclohexa-1,3-diene results in the formation of oxetans (I) and (II) in good yield.[†] Structural assignment of the *cis*- and *trans*-oxetans was made on the basis of their n.m.r. spectra. $J_{a,b}$ in the *cis*-isomer (II) is larger than that in the *trans*-isomer (I). Furthermore, the signal for H_a in (I) is at higher field than that in (II). This results from the fact that H_a in (I) is closer to the double bond. Actually the signal for H_a in the reduced trans-isomer (III) shifts to low field. Other conjugated dienes[‡] also gave oxetans in good yield.

The following routes are possible for oxetan formation: (i) Triplet propionaldehyde attacks the diene directly to produce the oxetan. (ii) The triplet diene which is produced by energy transfer from triplet propionaldehyde attacks ground-state propionaldehyde.[1] (iii) Excited singlet propionaldehyde attacks the diene.

The Figure shows Stern–Volmer plots of the quantum yields for the formation of oxetans and cyclohexadiene

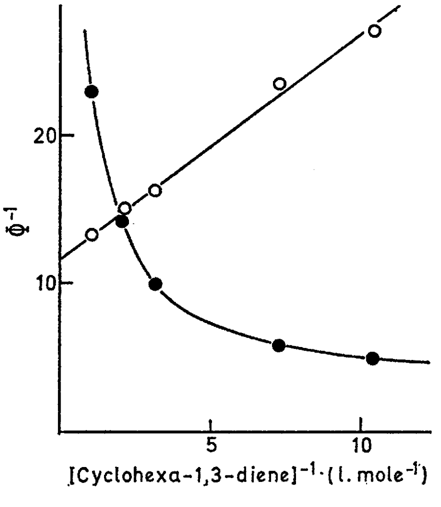


FIGURE. *Product yields as a function of [cyclohexa-*1,3-*diene*]$^{-1}$: ○, *oxetans*; ●, *dimers. Propionaldehyde* ($1\cdot09 \times 10^{-1}$ M) *in benzene*; >3100 Å.

[†] Dimers of cyclohexa-1,3-diene were also formed as minor products. The ratio of (I) to (II) was *ca.* 4. These products were isolated using a preparative g.l.c. and were characterized by i.r., n.m.r., and elemental analyses.

[‡] Piperylene, isoprene, 2,3-dimethylbutadiene and cyclopentadiene. Unpublished results.

dimers as a function of cyclohexa-1,3-diene concentration. The dimers decrease as the concentration of cyclohexa-1,3-diene increases. On the other hand, plots for oxetans are linear up to high concentration of cyclohexa-1,3-diene. This indicates that different precursors exist for the formation of oxetans and dimers. It is well known that dimers are formed *via* diene triplets.[2] Therefore, if oxetans were formed by mechanism (i) or (ii), dimers would have to increase with the concentration of cyclohexa-1,3-diene. This is incompatible with the results.§ Mechanism (ii) is also ruled out by the fact that oxetans are hardly obtained under conditions such as those under which triplet dienes are exclusively formed (phenanthrene-sensitized experiments). On the other hand, mechanism (iii) explains these results satisfactorily. That the line of oxetan formation does not give an intercept of 1 would indicate that the oxetan is formed *via* a singlet complex such as Turro and his co-workers have suggested.[3]

The following scheme is conceivable.¶

$$P_0 + h\nu \rightarrow P_1$$

$$P_1 \rightarrow P_0 + h\nu'$$

$$P_1 \rightarrow P_3$$

$$P_1 + \text{cyclohexa-1,3-diene} \rightarrow C_1$$

$$C_1 \rightarrow \text{oxetan}$$

$$C_1 \rightarrow P_0 + \text{cyclohexa-1,3-diene}$$

$$P_3 + \text{cyclohexa-1,3-diene} \rightarrow P_0 + \text{cyclohexa-1,3-diene}_3$$

$$\text{Cyclohexa-1,3-diene}_3 + \text{cyclohexa-1,3-diene} \rightarrow \text{dimer}$$

C_1: singlet complex

Little has been known about the photocycloaddition reactions of carbonyl compounds to conjugated dienes.[1,4] It is interesting that such reactions arise from the excited singlet state of propionaldehyde.

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§ The yield of cyclohexa-1,3-diene dimers decreases by *ca.* 20% in the presence of air, but the yield of oxetans is unchanged, so mechanism (i) can be excluded.

¶ This scheme is compatible with the observation that the fluorescence of propionaldehyde is quenched by added cyclohexa-1,3-diene.

[1] J. Saltiel, R. M. Coates, and W. G. Dauben, *J. Amer. Chem. Soc.*, 1966, **88**, 2745.

[2] D. Valentine, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1964, **86**, 5202.

[3] N. J. Turro, P. A. Wriede, and J. C. Dalton, *J. Amer. Chem. Soc.*, 1968, **90**, 3274.

[4] E. H. Gold and D. Ginsburg, *Angew. Chem.*, 1966, **78**, 207.