

***cis,trans*-1,1'-BICYCLOHEXENYL: A STRAINED GROUND STATE INTERMEDIATE IN THE PHOTOCYCLIZATION OF 1,1'-BICYCLOHEXENYL TO ITS ISOMERIC *cis*-CYCLOBUTENE<sup>†</sup>**

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### Summary

The mechanisms of the formation of the cyclobutene tricyclo[6.4.0.0<sup>2,7</sup>]-*cis*-7,8-dodec-1-ene (CB) and the ethers formed from 1,2- and 1,4-additions of methanol on direct and sensitized photoexcitation of 1,1'-bicyclohexenyl (BCH) have been investigated using steady state and transient methods. The existence of a ground state transoid intermediate, *cis,trans*-1,1'-bicyclohexenyl (*c,t*-BCH), was established by flash spectroscopic and kinetic observations. This transient absorbs in the 280 - 430 nm range ( $\lambda_{\max} = 360$  nm) and has a lifetime of 0.8  $\mu$ s at 23 °C in methanol that is independent of oxygen concentration. The decay of the intermediate is strongly temperature dependent,  $\ln k_d^0 = 27.8 - 8.15/RT$  ( $RT$  is in kilocalories per mole) in acetonitrile, and is accelerated by added acid,  $k_d = (1.17 \times 10^6 + 1.13 \times 10^8 [H^+]) s^{-1}$  in methanol. The effect of  $[H^+]$  on product quantum yields has also been determined. The results show conclusively that *c,t*-BCH is the only CB precursor following triplet sensitized excitation of BCH and accounts for 64% of CB formation when BCH is excited directly. *c,t*-BCH has also been shown to be the only photogenerated precursor to ethers. The dependence of ether quantum yields on methanol and acid concentration was determined.

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The *cis*-cyclobutene tricyclo[6.4.0.0<sup>2,7</sup>]-*cis*-7,8-dodec-1-ene (CB) is obtained as a major product from 1,1'-bicyclohexenyl (BCH) under direct [1 - 3] or sensitized [2, 3] excitation conditions. The exclusively *cis* stereochemistry [2] (based on a comparison of the nuclear magnetic resonance spectra of *cis*- and *trans*-CB [2, 4]) seemed to be consistent with its formation by a disrotatory process in either the lowest singlet or triplet excited state as predicted by the Woodward-Hoffmann (WH) orbital symmetry rules [5]. However, since adiabatic formation of either <sup>1</sup>CB\* or <sup>3</sup>CB\* would be highly

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<sup>†</sup> Dedicated to Professor Dr. Dietrich Schulte-Frohlinde on the occasion of his 60th birthday.

endothermic, Dauben *et al.* [2] explained the stereochemistry by proposing the intermediacy of excited states stabilized by partial (disrotatory) bond formation between C<sub>1</sub> and C<sub>4</sub> of the diene moiety. The elegant extension of the Woodward–Hoffmann considerations performed by van der Lugt and Oosterhoff [6] provided theoretical justification for this proposal for the singlet pathway, but no analogous stabilization for the triplet state has been predicted on theoretical grounds [7]. On the basis of work concerning the photocyclization of *cis,cis*-cyclooctadiene, Liu [8] suggested that <sup>3</sup>BCH\* may give *cis,trans*-1,1'-bicyclohexenyl (*c,t*-BCH) as a strained intermediate which could undergo conrotatory cyclization on the ground state surface to give CB. *c,t*-BCH has also been proposed as a precursor of the methyl ether 1,2-E (see below) as a specific case of the photoaddition of methanol to cyclohexenes [9]. Spectroscopic [10] and chemical [10, 11] evidence which conclusively demonstrated the photochemical formation of *trans*-1-phenylcyclohexene provided the incentive for this investigation of the viability of the *c,t*-BCH pathway to CB, particularly since BCH represented the single remaining example of a possible conversion of a 1,3-diene triplet to a cyclobutene.

The existence of the ground state transoid intermediate *c,t*-BCH was established by flash spectroscopy and kinetic observations. The laser flash spectroscopy apparatus was the same as that described in ref. 12 except that a KrCl excimer laser and a nitrogen laser (Lambda Physik EMG 500) were employed in this work. Direct excitation of BCH ( $2.0 \times 10^{-4}$  M) at 249 nm

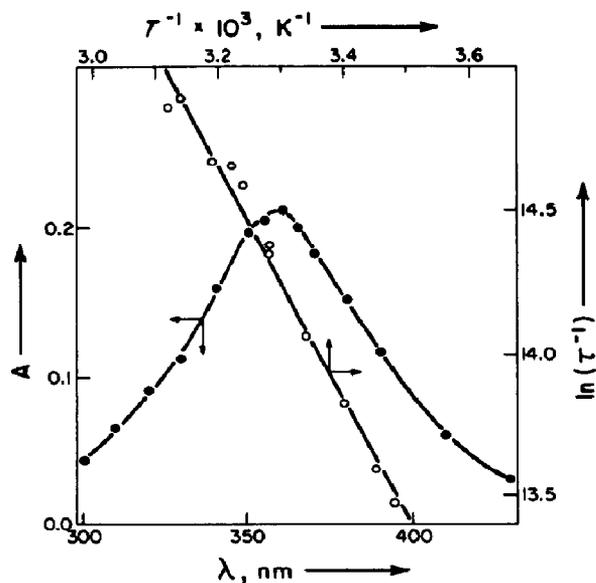


Fig. 1. ●, Absorption spectrum of *c,t*-BCH in methanol ( $[BCH] = 2.0 \times 10^{-4}$  M;  $\lambda_{exc} = 249$  nm;  $T = 23$  °C); ○, Arrhenius plot of the decay rate constant of *c,t*-BCH in acetonitrile ( $[BCH] = 0.07$  M;  $\beta$ -propionaphthone concentration such that  $A_{337} = 1.7$ ;  $\lambda_{exc} = 337$  nm,  $\lambda_{mon} = 365$  nm).  $\tau$  is in reciprocal seconds.

using a KrF excimer laser gives a single transient that develops within the excitation pulse period (less than 20 ns) and absorbs in the 280 - 430 nm range ( $\lambda_{\max} = 360$  nm) (Fig. 1). The transient lifetime (0.85  $\mu$ s, 0.95  $\mu$ s and 0.65  $\mu$ s at 23 °C in methanol, acetonitrile and cyclohexane respectively) is unaffected by oxygen. Upon sensitized excitation of BCH (0.05 M) using xanthone or  $\beta$ -propionaphthone as triplet energy donors ( $\lambda_{\text{exc}} = 337$  nm; nitrogen laser), the same transient is observed to grow in with a lifetime of about 45 ns which reflects most probably the lifetime of  $^3\text{BCH}^*$  and is, indeed, well within the range of lifetimes observed for 1,3-diene and olefin triplets [13]. The absence of an oxygen effect on the lifetime of the transient provides strong evidence that it is a ground state species. A threefold decrease in the lifetime would be expected for an electronically excited species with  $\tau_0 \approx 1$   $\mu$ s, if it is assumed conservatively that  $k_q[\text{O}_2] \approx 2 \times 10^6$   $\text{s}^{-1}$  [14, 15].

The temperature dependence of  $\tau_0$  was determined in acetonitrile ([BCH] = 0.07 M;  $\beta$ -propionaphthone;  $\lambda_{\text{exc}} = 337$  nm;  $\lambda_{\text{mon}} = 365$  nm). Least-squares analysis of the decay rate constants  $\tau_0^{-1}$  (Fig. 1) gives Arrhenius parameters  $E_a = 8.15 \pm 0.16$  kcal  $\text{mol}^{-1}$  and  $\ln A = 27.8 \pm 0.5$ , which compare well with the more approximate values of  $E_a = 7.5$  kcal  $\text{mol}^{-1}$  and  $\ln A = 24$  obtained for *trans*-1-phenylcyclohexene [10, 11].

The large spectral red shift (14 200  $\text{cm}^{-1}$ ) between the  $\lambda_{\max}$  values of the transient and *c,c*-BCH, which is almost identical with that observed for 1-phenylcyclohexene (14 300  $\text{cm}^{-1}$  [10]) and close to that reported for 1-acetylcyclohexene (15 000  $\text{cm}^{-1}$  [16]), also supports the conclusion that the transient is ground state *c,t*-BCH.

A further analogy with *trans*-1-phenylcyclohexene is provided by the observation of trapping by added sulfuric acid in methanol<sup>†</sup>. The linear relation between  $[\text{H}^+]$  and the decay rate constant

$$k_{\text{dt}} = \tau^{-1} = \tau_0^{-1} + k_p[\text{H}^+]$$

shown in Fig. 2 gives  $k_p = 1.1 \times 10^8$   $\text{M}^{-1} \text{s}^{-1}$ . This trapping with acid provides a convenient criterion for establishing the participation of *c,t*-BCH in CB formation. The simplest mechanism consistent with the CB formation quantum yields  $\phi_{\text{CB}}$  for the sensitized reaction is



<sup>†</sup>Sulfuric acid is a one-proton donor in methanol [17]. The reported protonation rate constant for *trans*-1-phenylcyclohexene [10, 11] must be multiplied by 2 for comparison with the value obtained here for *c,t*-BCH.



Steady state assumptions for all excited species and *c,t*-BCH lead to

$$\phi_{\text{CB}}^{-1} = (\phi_{\text{is}}\alpha\beta)^{-1}(1 + k_p\tau_0[\text{H}^+]) \quad (6)$$

where the symbols are defined in eqns. (1) - (5). Values of  $\phi_{\text{CB}}$  with benzophenone as sensitizer ( $\phi_{\text{is}} = 1$ ) in methanol with up to 0.01 M perchloric acid follow eqn. (6) (Fig. 2), giving  $(\alpha\beta)^{-1} = 94.1 \pm 2.8$  and  $k_p\tau_0 = 131 \pm 8 \text{ M}^{-1}$  at 30.0 °C<sup>†</sup>. The excellent agreement with  $k_p\tau_0 = 96 \pm 8 \text{ M}^{-1}$  obtained at 23 °C from the transient *c,t*-BCH data<sup>‡</sup> (Fig. 2) verifies Liu's proposal [8] that CB derives solely from *c,t*-BCH when triplet energy donors are employed.

If cation formation (eqn. (5)) were followed by irreversible trapping by methanol to give methyl ethers, as appears to be the case for 1-phenylcyclohexene [10], the fraction  $\alpha$  of <sup>3</sup>BCH\* which decays to *c,t*-BCH could be determined easily. The methyl ether 1,2-E obtained by Kropp *et al.* [9] from

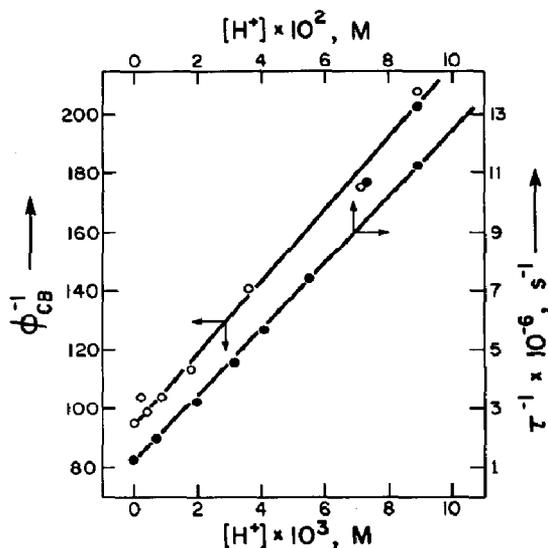


Fig. 2. Proton concentration dependence of the decay rate constants of *c,t*-BCH at 23 °C (●) and of  $\phi_{\text{CB}}$  (○) for the benzophenone-sensitized reaction at 30 °C. Both were measured in methanol solutions.

<sup>†</sup>A merry-go-round apparatus was employed [18] ( $\lambda_{\text{exc}}$  values of 366 nm and 254 nm (mercury lines) were used for sensitized and direct experiments respectively) and the *trans* → *cis* photoisomerization of stilbene was used for actinometry. The details are given in ref. 19.

<sup>‡</sup>This value was obtained by excluding the 0.073 M and one of the 0.089 M decay rate constants from the least-squares treatment. Inclusion of these points gives  $k_p\tau_0 = 128 \text{ M}^{-1}$  with some increase in uncertainty. Since both  $k_p$  and  $\tau_0$  are temperature dependent a small difference between the values of the transient and steady state treatments was expected.



the sensitized excitation of BCH corresponds to 1,2-addition of methanol to the diene. We have identified a second methyl ether 1,4-E, which is observed only when acid is excluded from the irradiation mixture ( $[1,2-E]/[1,4-E] = 3.3 \pm 0.4$ ). In inert solvents such as benzene or acetonitrile, the ether quantum yields increase sharply with methanol concentration. In the presence of acid 1,4-E reverts to *c,c*-BCH, and a thermal equilibrium favoring *c,c*-BCH is rapidly established between 1,2-E and *c,c*-BCH<sup>†</sup>. Light and the intervention of *c,t*-BCH shift the equilibrium towards 1,2-E, but the analysis of the data is complex and is best deferred to a subsequent paper. However, it can be stated that analysis of the ether quantum yields generally leads to the conclusion that (1)  $\alpha$  has a value of  $0.34 \pm 0.03$  or more which is characteristic of the decay of a twisted olefin triplet and (2) *c,t*-BCH is the sole photogenerated precursor of the ethers. The first of these conclusions implies that most of the inefficiency in CB formation is due to the small value of  $\beta$  in eqn. (4). Examination of the effect of acid on  $\phi_{CB}$  for direct excitation of BCH at 254 nm in methanol showed that 64% of CB is formed from *c,t*-BCH and the rest forms by an acid-independent path, presumably as a disrotatory process in the lowest excited singlet state surface. These results will also be presented in a subsequent paper.

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<sup>†</sup>See the first footnote of p. 370.

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