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K. C. Nicolaou,* W. E. Barnette, R. L. Magolda

Department of Chemistry, University of Pennsylvania
Philadelphia, Pennsylvania 19104

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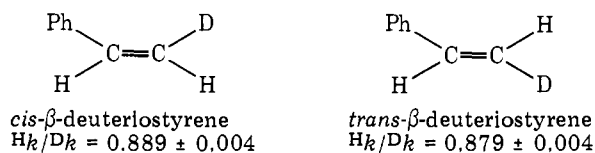
Carbon-14 and Deuterium Isotope Effects during the [2 + 2] Cycloaddition of Diphenylketene to Styrene¹

Sir:

It is well established² that concerted [2 + 2] cycloadditions of ketenes to alkenes proceed through crosswise transition states resembling the orientation complex shown in Figure 1. Two orbital symmetry-allowed mechanisms have been proposed²ⁿ for these reactions: (1) the [$\pi 2_s + \pi 2_a$] cycloaddition and (2) the [$\pi 2_s + \pi 2_s + \pi 2_s$ (or $\pi 2_s + \pi 2_a + \pi 2_a$)] mechanism. Both are compatible with the crosswise transition state.

Baldwin and Kapecki³ were among the first to adduce evidence that styrene and diphenylketene add in a concerted fashion by determining for the reaction the deuterium isotope effects for α - and β -labeled styrenes ($(^Hk/^Dk)_\alpha = 1.23$; $(^Hk/^Dk)_\beta = 0.91$ per deuterium, 65 °C). In their measurement of $(^Hk/^Dk)_\beta$, styrene- β,β - d_2 was employed, and $^Hk/^Dk$ per deuterium was calculated therefrom by taking the square root of the observed value. The latter ($(^Hk/^Dk)_\beta = 0.91$) is inverse, as expected⁴ for the $sp^2 \rightarrow sp^3$ hybridization change, but $(^Hk/^Dk)_\alpha = 1.23$ is unexpected, and has thus far not been explained.⁵

In an attempt to learn more about the reaction of styrene with diphenylketene, we prepared $Ph^{14}CH=CH_2$, $PhCH=^{14}CH_2$, $Ph_2^{14}C=C=O$, and $Ph_2C=^{14}C=O$, and measured⁶ $^{12}k/^{14}k$ for all four labeled species during the [2 + 2] addition. In addition we prepared⁷ the two forms of β -



deuteriostyrene and, using methods described before,⁶ determined the $^Hk/^Dk$ values for these two species as well, for we could deduce no reason—given the crosswise transition state—why $(^Hk/^Dk)_{cis}$ and $(^Hk/^Dk)_{trans}$ should be the same. The results of the four $^{12}k/^{14}k$ determinations are given in Figure 1. Also given (in Figure 1) is the average value for our determination of $(^Hk/^Dk)_{cis}$ and $(^Hk/^Dk)_{trans}$. The individual values for these two deuterium isotope effects are shown in the text under the appropriate structures, and to our surprise are identical within experimental error (they are also very close to the value determined by Baldwin and Kapecki³).

Heavy-atom isotope effects are partially understood through use of the Bigeleisen-Mayer expression,⁸

$$k_1/k_2 = \nu_{1L}^\ddagger/\nu_{2L}^\ddagger \left[1 + \sum_i^{3n-6} G(u_i) \Delta u_i - \sum_i^{3n-7} G(u_i^\ddagger) \Delta u_i^\ddagger \right] \quad (1)$$

and the relationship to transition-state structure developed by Fry⁹ and Sims.¹⁰ In eq 1, subscripts 1 and 2 refer to light and

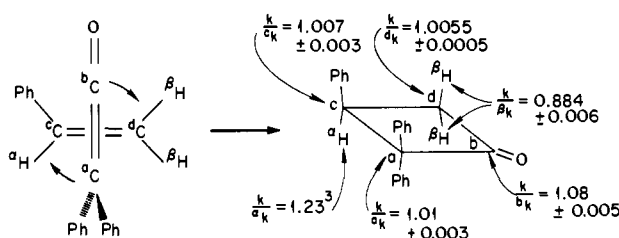


Figure 1.

heavy isotopes, respectively, $\nu_{1L}^\ddagger/\nu_{2L}^\ddagger$ is the ratio of the imaginary frequencies at the transition state (always > 1). Within the brackets are evaluations of the partition functions for reactant and activated complex. The terms u_i and u_i^\ddagger are vibrational frequencies, and Δu_i and Δu_i^\ddagger are the frequency shifts caused by isotope substitution. The negative term $\sum_i^{3n-7} G(u_i^\ddagger) \Delta u_i^\ddagger$ inside the brackets represents the effect of isotopic substitution on the vibrational frequencies of the transition state, and, the larger it becomes, the smaller the primary heavy-atom isotope effect will be. Equation 1 has been elegantly tested by Kresge and coworkers.¹¹ The Fry⁹-Sims¹⁰ work relates the structure of the transition state to the magnitude of the heavy-atom isotope effect—a relatively “symmetric” transition state (i.e., one with comparable bond orders for the weakening and forming bonds) corresponds to a larger k/k than one with substantially unequal bond orders. Applying both the Bigeleisen-Mayer⁸ and Fry⁹-Sims¹⁰ relations to our data, the large $^{12}k/^{14}k$ (1.08) for bC (Figure 1) is consistent with an activated complex in which there is (a) a highly polarized carbonyl group with a strongly negative^{4e} oxygen, (b) a substantial decrease in bonding at bC , and (c) a near balancing of old bond breaking and new bond making at aC , cC , and dC . The small carbon-14 isotope effects at aC , cC , and dC would then result from a balance of the weakening of the aC - bC and cC - dC bonds with a corresponding strengthening of the aC - cC and bC - dC bonds. The term $\sum_i^{3n-7} G(u_i^\ddagger) \Delta u_i^\ddagger$ must also be small.

The values for the $^Hk/^Dk$'s in the cycloadditions of *cis*- and *trans*- β -deuteriostyrenes to diphenylketene are inverse, as expected, and in accord with the Streitwieser¹¹ and Wolfberg-Stern⁴ treatments for α -deuterium isotope effects (to which these isotope effects in both the α and β positions of styrene belong), in which out-of-plane bending makes the largest contribution to the double differences in zero point energies between ground and transition states. That our values for the two β -deuteriostyrenes are nearly identical is consistent with a transition state in which diphenylketene exerts little compression on *cis* H or *trans* H owing to the two phenyls or the carbonyl oxygen. A transition state of the kind indicated in Figure 1 would satisfy this requirement, for the “naked” sp carbon at bC must exert negligible steric compression on the *trans*- β hydrogen (it is, in fact, the sp character of that carbon which makes the concerted [2 + 2] addition possible). The compression of the two phenyls at aC against the *cis*- β hydrogen must also be negligible, particularly when compared with the compression against the α hydrogen (which is flanked by three phenyls). In fact, aH must be seriously squeezed in the transition state which—presuming the Streitwieser⁴ explanation is operating—should make its isotope effect even more negative than that for the β hydrogens. This, of course, works in the wrong direction to explain the large (1.23) value observed³ for $(^Hk/^Dk)_\alpha$. Thus we conclude that another factor which works in the opposing direction must be called into play, and the special kind of hyperconjugation suggested by Baldwin and Kapecki³ is the best explanation available at this time.

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Clair J. Collins*

Oak Ridge National Laboratory, Oak Ridge, Tennessee
and the Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37916

Ben M. Benjamin

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

George W. Kabalka

Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37916

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Effects of Liquid Crystal Solvents on the Photodimerization of Acenaphthylene

Sir:

The effects of media on thermal and photochemical reactions have received much attention in recent years. The utility

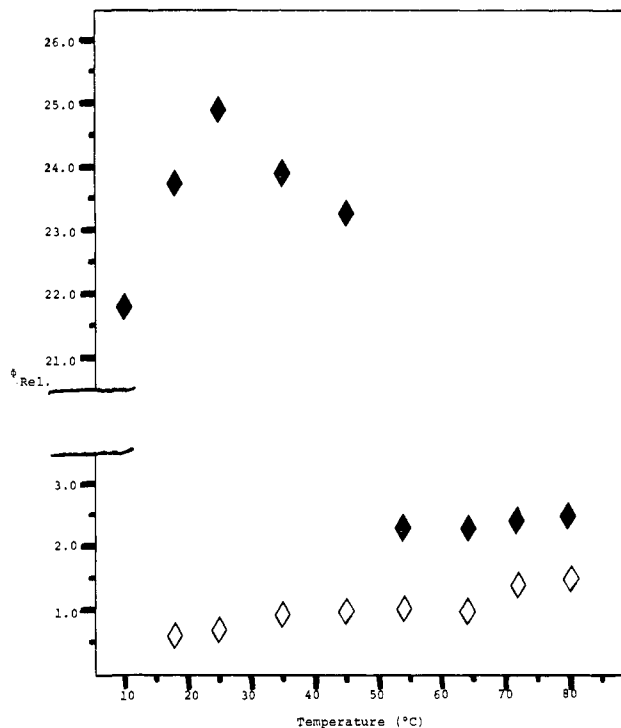
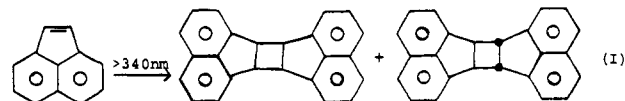


Figure 1. Φ_{Rel} vs. temperature for dimerization of 0.08 M acenaphthylene in *n*-butyl stearate (\diamond) and the cholestanyl ester mixture (\blacklozenge). Φ_{Rel} is defined as $\Phi_{\text{solvent}}/\Phi_{\text{toluene}}$ at each temperature. Each point is the average of at least duplicate measurements.

of monolayers,¹ micelles,² and, in particular, liquid crystals³ to probe environmental influences on chemical reactivity has been demonstrated.

Here, we report what we believe to be (1) the largest rate enhancement of any bimolecular reaction conducted in a liquid crystal, and (2) the first example of a pitch controlled reaction rate in a cholesteric phase.⁴

The photodimerization of acenaphthylene is known⁵ to yield its *syn*- and *anti*-cyclobutane dimers (eq I). The product dis-



tribution has been suggested to be state and solvent dependent.⁶ Quantum yields and product distributions⁷ have been determined here in toluene, *n*-butyl stearate, and a 1:1 mixture of 5 α -cholestan-3 β -yl acetate and 5 α -cholestan-3 β -yl nonanoate⁸ as a function of temperature, solvent phase, and concentration of starting material. Nitrogen saturated samples in sealed Pyrex capillary tubes were thermostated and irradiated ($\lambda > 340$ nm) to 10-15% conversion in a miniature merry-go-round apparatus. Analyses of percent conversions (and, in some cases, product distributions) were performed conveniently by UV spectroscopy.⁹

The relative quantum yields for the dimerization of 0.08 M acenaphthylene in the three solvents as a function of temperature are shown in Figure 1. Absolute quantum yields¹⁰ for dimerization ($\sim 10\%$ conversion) of 0.08 M acenaphthylene at 366 nm in toluene are 0.011, 0.012, and 0.012 at 25, 35, and 55 $^{\circ}\text{C}$, respectively. The quantum yield obtained at 25 $^{\circ}\text{C}$ is near the value (0.0135) reported by Livingston and Wei^{5b} for reaction under conditions similar to ours.

As can be seen, the quantum efficiency in *n*-butyl stearate (Φ_s), which exhibits a smectic phase below 25 $^{\circ}\text{C}$,¹¹ varies slightly as a function of temperature and remains near the efficiency observed in toluene solutions (Φ_t). This similarity is unexpected if solvent viscosity alone determines the dimer-