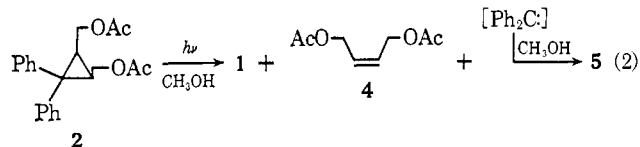


covered **2** (eq 2). The formation of olefins **3** and **4** was also observed in ether and cyclohexane (gc).



Triplet sensitization of **1** and **2** with xanthone afforded no detectable amounts of **3** and **4**. Net isomerization of each cyclopropane to the other isomer was observed, indicating transfer of triplet energy from the xanthone to the cyclopropanes had occurred. This indicates that the pathways leading to fragmentation of **1** and **2** do not involve the triplet states of these molecules.

The preparative irradiations gave an indication of reaction stereospecificity. This was confirmed by low conversion experiments. Irradiation of 0.13 *M* ether solutions of **1** and **2** were carried out to give less than 1% conversion to the other cyclopropane stereoisomer. At this point analyses for olefins **3** and **4** were carried out.¹⁰ These revealed that cyclopropane **1** yielded olefin consisting of at least 99% **3**. Similarly, **2** produced >99% **4** at these very low conversions. As the photolyses proceeded further and the amount of the other cyclopropane stereoisomer increased, the percentage of the other olefin likewise increased as expected. Thus, the fragmentations of **1** and **2** are essentially completely stereospecific.¹¹

Relative quantum yields for isomerization and cleavage of **1** and **2** were measured on a merry-go-round apparatus at the same very low (<1%) conversions. These experiments yielded for *cis*-cyclopropane **2** $\phi_{\text{isom}}/\phi_{\text{cleav}} = 4.6 \pm 0.2$, and for *trans*-cyclopropane **1** $\phi_{\text{isom}}/\phi_{\text{cleav}} = 1.1 \pm 0.1$. The data also reveal that **2** cleaves more efficiently than does **1**: $\phi_2/\phi_1 = 2.6 \pm 0.2$. It should be noted that these ratios of quantum yields for isomerization *vs.* fragmentation for each cyclopropane isomer are maximum figures for the relative rates of the two processes from the singlet states of **2** and **1**, since the triplet contribution to isomerization is not known in either case.

These results indicate that the fragmentation process proceeds *via* the singlet state bypassing any long-lived intermediate diradical (excited state or ground state) species having free rotation about the terminal carbons. Similarly, carbene formation *via* thermal cleavage of diradicals with the 0,0 geometry formed by disrotatory photochemical ring opening¹ cannot account for the product stereochemistry. Instead, the reaction appears to be a concerted, allowed excited state process. It is conceivable that fragmentation occurs from a singlet state other than the spectroscopic one—a state⁶ having one or more ring bonds considerably stretched relative to the ground state. Our results then provide certain restrictions on this state with respect to geometry, rotational barriers, and mode of cleavage.

(10) Analyses for olefins and cyclopropanes were carried out with a Perkin-Elmer Model 990 gas chromatograph equipped with a flame ionization detector. For **3** and **4** a 7 ft \times 1/8 in. stainless steel column packed with 10% C-6 diethylene glycol succinate on Anakrom S.D., 90–100 mesh operated at 130°, was used. Cyclopropanes were analyzed on a 5 ft \times 1/8 in. stainless steel column packed with 3% XE-60 on Varaport 30, 100–120 mesh operated at 195°. Yields were determined with an internal standard.

(11) Experiments in which **4** was added to **1** and **3** to **2** prior to photolysis showed no detectable loss of **4** or **3**, respectively. Thus the observed stereospecificity cannot be due to selective destruction or isomerization of the nonobserved olefin.

We note that this stereospecificity is especially interesting in light of the fact that the thermal reverse of the fragmentation—the addition of singlet carbenes to olefins¹²—is likewise highly stereospecific and probably concerted. The difference between the thermal and photochemical reactions would appear to lie in the relative orientation of carbene and olefin during reaction.^{7a,13}

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Stephen S. Hixson

Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01002

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¹⁴C Isotope Effects in the 1,3-Dipolar Addition of *N*, α -Diphenylnitron and Styrene. A Concerted Cyclic Process¹

Sir:

We find that the primary carbon-14 kinetic isotope effects² in the 1,3-dipolar addition of *N*, α -diphenylnitron^{3,4} and styrene to yield 2,3,5-triphenylisoxazolidine are consistent with Huisgen's^{5,6} concerted, cyclic mechanism and inconsistent with the diradical mechanism.^{7–9}

Inter-¹⁰ and intramolecular¹¹ deuterium isotope effects have been used in attempts to answer the question of concerted *vs.* diradical addition during 1,3-dipolar additions, but with indifferent results.

We prepared PhCH=N(O)Ph, PhCH=CH₂, and PhCH=CH₂ by standard methods^{3,12} and, in separate experiments, determined the isotope effects during the additions. In these measurements, the method of competing reactions and low conversion¹³ was employed, except during the experiments with *N*, α -diphenylnitron and styrene- α -¹⁴C, for which a variation of the differential method¹⁴ was used. The reactions all took place in boiling ethanol containing a trace of hydroquinone to suppress styrene polymerization. The results are shown in Figure 1 and leave no doubt, we believe, that the reaction must proceed through a

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

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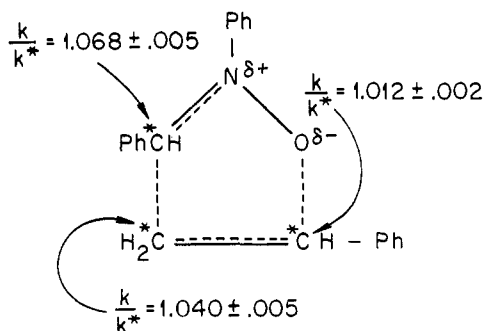


Figure 1.

cyclic transition state such as that symbolized. If the mechanism were to proceed instead through one of the diradicals **1** or **2**, the carbon atoms containing the odd



electrons at the diradical stage would remain sp^2 hybridized, as they were in the reactants, and we would expect two carbon-14 isotope effects for one bond in the formation of **1**, or a single carbon-14 isotope effect¹⁵ for the other bond in the formation of **2**. In the diradical mechanism, however, we would not expect carbon-14 isotope effects during the formation of both bonds except under circumstances requiring *both* **1** and **2** as intermediates, a condition rejected unequivocally by Firestone,¹ who states that nitrones react through diradicals of type **1**. The smallest ($k/k^* = 1.012 \pm 0.002$) of the three ratios shown in Figure 1 is larger than any known *secondary* isotope effect¹⁴ of carbon-14 and, in addition, is not less than unity, but in the normal direction.

It is interesting, but not unexpected,^{2,16,17} that the isotope effects exhibited at each of the two carbons involved in making the single C-C bond (Figure 1) are substantially different. The difference in k/k^* for the α -¹⁴C- and β -¹⁴C-labeled styrenes does not necessarily mean that bond formation associated with the smaller value lags formation of the other bond. The situation is more complicated than this, and has been discussed by Fry² and Van Hook¹⁶ in terms of the Bigeleisen-Mayer expressions.¹⁷

Acknowledgment. We wish to thank Dr. Vernon F. Raaen for independent analyses of certain of the labeled samples.

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Ben M. Benjamin, Clair J. Collins*

Chemistry Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

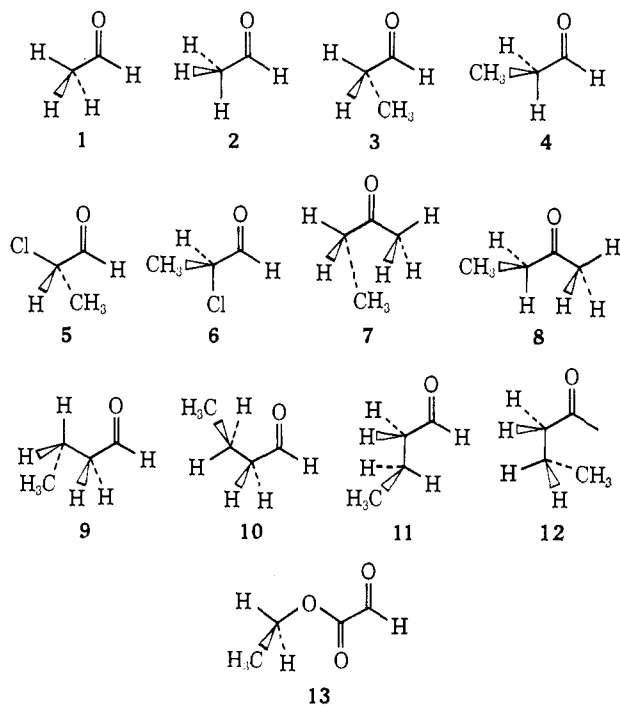
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Orbital Factors and Asymmetric Induction

Sir:

We suggest that, *at least partially*, orbital factors may be responsible for asymmetric induction. An asymmetric center induces a hybridization change in a vicinal unsaturated system. A dissymmetric π -electron cloud results and the reactivity of the two diastereotopic faces toward an ionic reagent will not be the same.

Ab initio (STO-3G) calculations¹ have been performed for the following molecules: acetaldehyde, propanal, 2-chloropropanal, butan-2-one, butanal, and ethyl glyoxylate. Two fixed conformations are considered for acetaldehyde (**1** and **2**), propanal (**3** and **4**), 2-chloropropanal (**5** and **6**), butan-2-one (**7** and **8**), four fixed conformations for butanal (**9**-**12**), and one for ethyl glyoxylate (**13**). Standard geometries are used throughout.



The principal results are the following. (1) A σ - π mixing occurs in the carbonyl group of compounds **3**-**13**. For example, whereas the π orbital of acetaldehyde contains only 10^{-10} 2s character, the same orbital in **3** incorporates up to 10^{-3} 2s character. In some other orbitals, the σ - π mixing is even greater. Thus, in the 11th occupied molecular orbital (MO) of **3**,² the coefficients of the carbonyl group are: 0.354 (2s) and 0.104 ($2p_z$) for the oxygen atom and -0.160 (2s) and 0.134 ($2p_z$) for the carbon atom.

(2) As anticipated, the π -electron cloud becomes dissymmetric: the electron density is greater on one diastereotopic face than on the other. It seems reasonable to suppose that a nucleophilic reagent would attack preferentially on the positive face. An aldehyde may react under several conformations. In accordance

(1) It is known that *ab initio* calculations with the minimal basis set give fairly good results for charge distribution; the calculated dipoles are usually smaller than the experimental values but the general trends are well reproduced. See, for example, W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2191 (1970); W. J. Hehre, L. Radom, and J. A. Pople, *ibid.*, **94**, 1496 (1972).

(2) The numbering starts from the lowest MO.