Table I. Results of Quenching of Ketone Triplets[a]

Ketone (E_T, kcal)	$k_q\tau_0$[b]	$k'_q\tau_0$[c]	k_q/k'_q
II, R = ethyl	0.29 ± 0.01[d]	0.019 ± 0.001	15.3
R = isobutyl	0.29 ± 0.01	0.021 ± 0.002	13.8
R = isoamyl	0.32 ± 0.02	0.031 ± 0.002	10.3
R = *n*-butyl	0.59 ± 0.04	0.048 ± 0.003	12.3
R = methyl	0.71 ± 0.02	0.075 ± 0.004	9.5
α-Santonin, I (68 ± 1)[e]	0.40 ± 0.06	0.096 ± 0.009	4.2
	(0.22 ± 0.02)[f]	(0.075 ± 0.005)[f,g]	(2.95)[f]
III (61–69)[h]	0.57 ± 0.04	0.24 ± 0.03[i]	2.4
II, R = H	2.31 ± 0.14	0.80 ± 0.02	2.9
IV (67 ± 1)[j]	10.7 ± 0.3	6.95 ± 0.33[k]	1.5
V (63 ± 1)[h]	34.1 ± 0.5	25.2 ± 1.2	1.35
VI (60 ± 1)[h]	107.1 ± 1.4	112.4 ± 6.0	1.0
Cyclopentenone (61 ± 1)[l]			
0.12 *M*	11.0 ± 0.6	14.0 ± 0.5	0.79
1.0 *M*	8.1 ± 0.3	9.6 ± 0.3	0.85
3.0 *M*	4.6 ± 0.1	4.5 ± 0.3 (5.0)[m]	1.02
6.1 *M*	2.1 ± 0.1	2.2 ± 0.1	0.96

[a] Determined by a competitive irradiation technique using a merry-go-round apparatus, high-pressure mercury lamp, Pyrex filters, benzene solutions, room temperature. Conversions in the blank were kept generally under 5% (and in no case beyond 15%) to prevent light absorption by products. In certain cyclohexadiene runs, the 366-nm line was isolated with a Corning 7-83 filter combination, and no difference was observed from runs with Pyrex filters. Analysis for product appearance by glpc with flame ionization detection using internal standards and calibration with known mixtures of reactant, products, and standard. [b] Quenching with 1,3-cyclohexadiene. [c] Quenching with *trans*-piperylene. [d] Standard deviation from least-squares straight line. Accuracy is estimated at better than 10%, from repeat determinations. [e] From emission spectra: ref 3 and M. H. Fisch and J. H. Richards, *J. Am. Chem. Soc.*, **85**, 3029 (1963). [f] Repeat determination at 366 nm using a different analytical technique. [g] *cis*-Piperylene, slope = 0.094 ± 0.004. [h] From studies with a graded series of sensitizers and quenchers. [i] Commercial mixture of *cis*- and *trans*-piperylenes. [j] From emission spectra: D. J. Patel and D. I. Schuster, *J. Am. Chem. Soc.*, **89**, 184 (1967), and H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *ibid.*, **89**, 6589 (1967). [k] *cis*-Piperylene, slope = 6.0 ± 0.3. [l] By chemical spectroscopy and phosphorescence quenching.[11,12] [m] Reference 4.

to cyclohexadiene and k' to *trans*-piperylene, and k_{et} is the rate constant for the process $(D^* + A) \rightarrow D_0 + A^*$.[10]

From the relationship $k_q = \alpha k_{dif}$, where

$$\alpha = \frac{k_{et}}{k_{et} + 1/\tau_0 + k_{-dif}}$$

we have

$$\frac{k_q}{k'_q} = \frac{\alpha}{\alpha'} = \frac{k_{et}}{k'_{et}}\frac{(k'_{et} + 1/\tau_0 + k_{-dif})}{(k_{et} + 1/\tau_0 + k_{-dif})} = \frac{k_{et}}{k'_{et}}(1 - \alpha\beta) = \frac{1 - \alpha\beta}{1 - \beta}$$

where $k'_{et} = k_{et}(1 - \beta)$.

For long-lived triplets, $1/\tau_0$ is very small compared with k_{et} and k_{-dif}, so that α is independent of triplet lifetime, but for triplets of lifetime on the order of 10^{-10} sec, the terms are of comparable importance and α becomes a function of lifetime. The value of k_q/k'_q will increase as τ_0 and α decrease, approaching a limiting value of k_{et}/k'_{et}. According to this treatment, differential quenching should be observable if $\beta \neq 0$ with long-lived triplets whenever $\alpha \neq 1$, although as pointed out previously[10] these effects may be lost beneath the large experimental error often associated with such measurements, especially when α is close to unity.[15] Furthermore, this treatment requires that even for short-lived triplets $k_q = k'_q$ if $k_{et} = k'_{et}$, *i.e.*, if $\beta = 0$. The reason why $k_{et} \neq k'_{et}$ for the ketones in Table I is not established with certainty but may be associated with an orientational effect such as preferential energy transfer to a cisoid rather than a transoid or skew diene, perhaps due to orbital overlap. This should be clarified by work in progress with an extensive series of ketones and dienes in a variety of solvents, which may provide information on the preferred orientation of donor and acceptor in such a process. The generality of these observations remains to be seen.[16]

Acknowledgment. We are grateful to Professor Peter Wagner for providing details of his work prior to publication, and to him and Professor Graham Underwood of this department for stimulating and helpful discussions.

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(15) The assumption is made throughout that energy transfer is exothermic by at least 3 kcal/mol.

(16) A case of a steric effect in "exothermic" energy transfer has been noted by W. G. Herkstroeter, L. B. Jones, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4777 (1966).

(17) Fellow of the Alfred P. Sloan Foundation.

(18) American Cyanamid Summer Fellow, 1965; Frederick W. Miller, Jr., Fellow, 1967.

(19) National Science Foundation Predoctoral Trainee, 1967.

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A Novel Probe into the Simultaneity of Cycloaddition Reactions. The [2 + 2] and [2 + 4] Systems

Sir:

In spite of the tremendous amount of work that has been devoted to the mechanism of [2 + 4] cycloaddition reactions, the problem of the simultaneity of these processes still demands a great deal of attention from mechanistic organic chemists. While most of the experimental literature seems to favor a synchronous process,[1] and Woodward and Hoffmann predictions clearly concur with this point of view,[2] there are notable cases where evidence points to a nonsynchronous

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Table I. Reaction of 1,1-Dideuterioallene with Acrylonitrile[a]

Run	Temp, °C	Reaction time, hr	Allene deuterium content[b,c]	Nmr ratio, allyl/vinyl	k_H/k_D cor[f]
1	210 ± 4	12	100% d_0	2.50 ± 0.02[d]	
2	206 ± 5	10	91.2% d_2 7.03% d_1	4.28 ± 0.03[e]	1.21 ± 0.02
3	225 ± 1	12	92.2% d_2 5.90% d_1	4.18 ± 0.04[e]	1.15 ± 0.02
4	225 ± 1	14	92.2% d_2 5.90% d_1	4.14 ± 0.05[e]	1.13 ± 0.02

[a] Reactions, using benzene as solvent, were run in sealed tubes and heated in a tube furnace. [b] Deuterium content was measured by low-voltage mass spectrometry. [c] Deuterium content of allene recovered from reaction mixture was virtually unchanged. [d] The chemical shift of the hydrogen α to the nitrile group is identical with that of the allyl hydrogens. [e] For an equimolar mixture of **2a** and **2b** one would expect an nmr ratio of 4.0. [f] The calculated isotope effect is corrected for d_1 content.

Table II. Reaction of 1,1-Dideuterioallene with Hexachlorocyclopentadiene[a]

Run	Temp, °C	Reaction time, hr	Allene deuterium content	Nmr ratio, allyl/vinyl[b]	k_H/k_D cor
1	150 ± 3	12	100% d_0	1.006 ± 0.006	
2	150 ± 3	15	91.2% d_2 7.03 % d_1	0.894 ± 0.004	0.89 ± 0.01
3	145 ± 2	12	91.2% d_2 7.03% d_1	0.87 ± 0.01	0.87 ± 0.01
4	145 ± 2	15	91.2% d_2 7.03% d_1	0.93 ± 0.01	0.93 ± 0.01
5	135 ± 1	12	91.2% d_2 7.03% d_1	0.923 ± 0.004	0.92 ± 0.01

[a] Reactions were run neat, in sealed tubes, and were heated in a tube furnace. [b] Heating the product mixture at temperatures as high as 200° caused virtually no change in the nmr ratio.

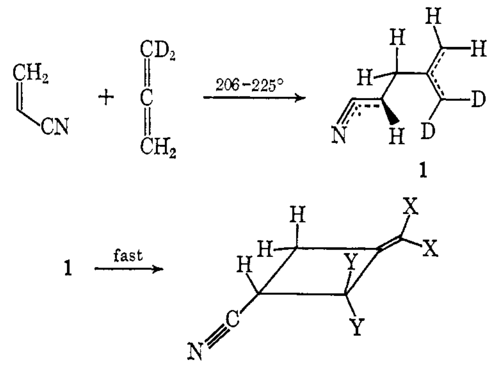
mechanism.[3-5] Indeed it has begun to seem likely that a range of mechanisms may actually exist, with a completely symmetrical transition state at one end of the scale, and a fully developed two-step mechanism at the other.

We wish to report results from an investigation, utilizing secondary deuterium kinetic isotope effects, in which we are able to contrast *directly* the [2 + 2] and [2 + 4] cycloaddition mechanisms. By means of this novel method we are able to contribute substantive support for the two-step nature of the former reaction and the concerted nature of the latter. This method promises to offer a general method for probing the simultaneity of many other cycloaddition reactions as well.

Secondary deuterium isotope effects have been utilized previously in careful investigations of both the [2 + 4] and [2 + 2] cycloaddition mechanisms.[6-8] However, in none of these cases was there available for observation an actual closely analogous model system for the *alternative* mechanism, and thus much of the impact of these studies was lost.

The novelty of our investigation is derived from the unique nature of allene as an adding species. The orientation of addition of allene to unsymmetrical species in [2 + 2] cycloadditions[9] makes it clear that, in a two-step process, initial bond formation would be at C_2, thereby creating an allyl radical. In such a process, the hybridization at C_1 and C_3 remains sp^2 and thus, if 1,1-dideuterioallene were used, little secondary deuterium isotope effect would be expected for this rate-determining step. The subsequent rapid ring closure, however, would likely exhibit a substantial intramolecular secondary deuterium isotope effect. In direct analogy to Crawford's study of the trimethylenemethane diradical,[10] the dideuteriomethylene would be expected to rotate significantly slower in ring closure than methylene itself.

In the reaction of acrylonitrile with 1,1-dideuterioallene[9,11] to give **2a** and **2b** in 60% yield, these expectations were realized, as shown in Table I.



1

2a, X = D; Y = H
b, X = H; Y = D

Thermal isomerization to an equilibrium mixture, *via* a degenerate methylenecyclobutane type of rearrangement,[12] is found to occur slowly under the reac-

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(10) R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966).

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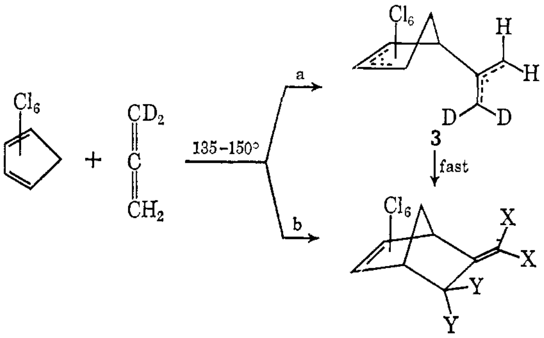
(12) W. von E. Doering and J. C. Gilbert, *Tetrahedron Suppl.*, **7**, 397 (1967).

tion conditions.[13] Thus the actual kinetic isotope effect is probably even larger than the largest value observed, 1.21.



4a, X = D; Y = H
b, X = H; Y = D

In the [2 + 4] cycloaddition reaction of hexachlorocyclopentadiene with 1,1-dideuterioallene to produce adducts **4a** and **4b** in 80% yield,[14] the observed kinetic deuterium isotope effect, k_H/k_D, was determined to be 0.90 ± 0.03 (see Table II).

This value is entirely consistent with a rate-determining change of hybridization from sp^2 to sp^3 at C_1 or C_3, and thus is, of course, consistent with a synchronous pathway for the reaction.

The fact that such obvious differences in k_H/k_D are found for the two different reactions is certainly strong evidence for a difference in mechanisms. The results for the [2 + 2] cycloaddition happily are consistent with past investigations which have shown the reaction to be nonsynchronous.[15] In the case of the [2 + 4] cycloaddition, in spite of the fact that the hypothetical intermediate diradical would be relatively quite stable, the evidence is certainly most consistent with a concerted mechanism. The two conclusions reinforce each other.

Of equal importance is the probability that this technique will prove to be an extremely sensitive probe into the simultaneity of any cycloaddition reaction in which allene may be a reactant.

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[13] After 25 hr at 270° complete equilibrium is observed.

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Model Ligands for Square-Planar and Square-Pyramidal Complexes[1]

Sir:

We wish to report the chelate stereochemistry of an unusual new tetradentate ligand, 1,5-diazacyclooctane-N,N′-diacetate (dacoDA). The stereochemistry of chelated 1,5-diazacyclooctane (daco) and 1,4-diazacycloheptane (dach, homopiperazine)[2] suggested that these ligands could be used to design a series of relatively simple tetradentate ligands which would lead to the formation of planar and, in the case of the daco derivatives, square-pyramidal (with an additional ligand) complexes. These ligands, daco(N–R)$_2$ and dach(N–R)$_2$, R = $-CH_2CO_2^-$ or $-CH_2CH_2NH_2$, should coordinate in a plane since coordination of the two tertiary amines in the eight-membered ring restricts the R groups to such an extent that the two five-membered chelate rings can form only in the plane defined by the metal ion and the two nitrogens (Figure 1). In order to attain axial coordination a great amount of strain has to be introduced into the chelate framework. Furthermore, because of strong nonbonding interactions between the methylene protons on the backbone portions of the tetradentate ligands based on daco when both halves of the chelated eight-membered ring are folded back away from the metal ion, it was expected that one-half of the ring would fold toward the metal ion, placing one of the β-methylene protons over an axial position. This would effectively block coordination at this position as shown in Figure 1. Such appeared to be the case for complexes prepared from the parent daco molecule.[2]

We have now shown these predictions[3] to be correct for the Ni(II)–dacoDA complex. We have determined the structure of $[Ni(dacoDA)(H_2O)]\cdot 2H_2O$ through X-ray crystallography and have found the solid-state geometry of the complex to be close to square pyramidal. In addition, experimental evidence suggests that this structure is maintained in aqueous solution. This is generally not the case for other five-coordinate complexes.[4]

Three-dimensional X-ray diffraction data were obtained using a Picker diffractometer with Mo Kα radiation. Green $[Ni(dacoDA)(H_2O)]\cdot 2H_2O$ crystallizes in the space group $P2_1/c$ with four molecules per unit cell. The lattice constants are a = 14.412, b = 7.316, and c = 14.431 Å with β = 112.92°. A Patterson map was used to locate the positions of the nickel atoms, and a series of Fourier syntheses was then used to locate the remaining atoms. A full-matrix least-squares refinement on 1600 reflections resulted in an R value of 8%.

The details of the structure determination will be published on completion of the study. Figure 1 gives a perspective of $Ni(dacoDA)(H_2O)$ with ligand-to-metal bond lengths and some pertinent bond angles. The nickel atom is located out of the plane about 10° toward the coordinated water. The complex is somewhat distorted from the idealized C_s symmetry expected from molecular models. The two remaining water oxygens (not shown in the figure) are 4.28 and 4.30 Å from the nickel which removes any possibility of coordination to the nickel.

The chelating properties of dacoDA were compared with those of ethylenediamine-N,N′-diacetate (EDDA) which has essentially the same crystal-field strength as dacoDA but should not sterically restrict a metal ion from attaining six-coordination, and it has been found

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(1) This work was supported in part by the Petroleum Research Fund (Grant No. 3153-A3) and by a grant provided for biological and medical research by the State of Washington Initiative Measure No. 171.

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