Table II. Emission Maxima (λem), Relative Fluorescence Quantum Yields  $(\phi_{rel})$ , Fluorescence Lifetimes  $(\tau_f)$ , Rotational Correlation Times  $(\tau_r)$ , and Polarization (p) for Merocyanine  $540^a$  in Various Media

medium	λ <sub>em</sub> , nm	$\phi_{ ext{rel}}{}^{b}$	$\tau_{\mathbf{f}}$ (±0.2),	$ au_{\mathbf{r}} \ (\pm 0.2), \\  ext{ns}$	$\langle p \rangle^c$ $(\pm 0.01)$
H <sub>2</sub> O	572	1.0	1.3	16.7	0.36
1-pentanol	582	4.5			
SDS (84 mM)	585	7.8	3.0	19.1	0.28
60% SCS microemulsion	584	8.0	2.8	19.3	0.29
CTAB (7.27 mM)	586	12.3			
60% CTAB microemulsion	584	12.0			
ethanol	583	7.8	2.4	15.3	0.28

 $<sup>^{</sup>a}$  Optical density of the solution at the excitation wavelength is about 0.06 in all the media.  $^{b}$   $\phi_{rel} = quantum yield in medium/$ quantum yield in H2O; absolute quantum yield of dye in H2O is 0.05.  $^{c}\langle p\rangle$  is the average value in the range 530-610 nm. The value of  $p_0$  determined in glycerol is 0.50  $\pm$  0.01.

## concentrations below 0.45 mM in 60% SCS.

Emission maxima ( $\lambda_{em}$ ), relative fluorescence quantum yields  $(\phi_{\rm rel})$ , fluorescence lifetimes,  $(\tau_{\rm f})$ , rotational correlation times  $(\tau_{\rm r})$ , and polarization (p) for the dye are summarized in Table II. Parallel to the shift in absorption maxima,  $\lambda_{em}$  are also red-shifted (ca. 10 nm) in organized media. In addition, the fluorescence quantum yields are considerably higher in microemulsion than in water. Normal micellar solutions also produced similar results. The yields are somewhat higher in cationic aggregates compared to those of the anionic ones. It should also be noted that the solubility of the dye in the microemulsion is much greater than in any of the components of the microemulsion. This is consistent with the solubilization of dye in the interfacial region of the microdroplet, in accord with the spectral data. 9,10 The solubility in ethanol is somewhat less than that in the microemulsion. If the actual volume of the interphase is taken into account (35% of the total volume), then the solubility becomes 30 mM in this region.

The enhancement of fluorescence yield in organized assemblies is normally due to either a microviscosity or a micropolarity<sup>11,12</sup> effect. A direct means to investigate these effects is to measure polarizations (p) and rotational correlation times  $(\tau_r)$ . If the increase in the fluorescence quantum yield is due to a microviscosity effect, then both p and  $\tau_r$  are expected to be significantly higher in organized media than in water. However, the data presented in Table II indicate that both p and  $\tau_r$  values in microemulsions are comparable to those in water. Therefore, it may be concluded that the high quantum yields in organized media are due to an effect of micropolarity and not of microviscosity. The dye experiences a micropolarity in microemulsions comparable to that in ethanol. This is corrobrated by the fact that  $\lambda_{em}$ , p, and  $\tau_r$  in ethanol are almost the same as those in microemulsion.

Irradiation of an aqueous solution of dye (1.74  $\mu$ M) with white light from a 450-W Xe lamp fitted with a Corning 360-nm cutoff filter resulted in a colorless solution in about 20 min. Under identical conditions, photobleaching of the dye was negligible (<3%) in alcohols and micellar solutions, and no photobleaching was observed in microemulsion. However, the photostability of dye to unfiltered white light depended on the medium. In water and 1-pentanol the dye degraded completely in less than 5 min and in about 20% ethanol and SDS solution, over a period of 70 min. In contrast, there was no detectable degradation of the dye in microemulsion. Therefore, unlike the other media, microemulsion is unique in maintaining the photostability of the dye under the experimental conditions employed in this study. The reasons for the enhanced photostability of the dye in microemulsion

In summary, the increased fluorescence quantum yield of merocyanine 540 in microemulsion and aqueous SDS micelles is due to the micropolarity rather than the microviscosity. Microemulsion is superior to ethanol or aqueous micellar solution in terms of dye solubility and photostability. Similar behavior has been noted for the cyanine dye 3,3'-dihexyloxacarbocyanine iodide.

Acknowledgment. We are thankful to Dr. Jane Vanderkooi (Department of Biochemistry and Biophysics, University of Pennsylvania) for helpful discussions and making available her facilities for all measurements of the present work. This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy.

Registry No. Merocyanine 540, 62796-23-0; sodium cetyl sulfate, 1120-01-0; cetyltrimethylammonium bromide, 57-09-0; sodium dodecyl sulfate, 151-21-3.

## gem-Alkylcyclopentadienes. 2. Secondary Deuterium Kinetic Isotope Effect Study of the Cycloaddition of Diphenylketene and 5,5-Dimethylcyclopentadiene<sup>1,2</sup>

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> > Received January 26, 1983

Ketenes<sup>3</sup> react with alkenes to yield cyclobutanones;<sup>4-6</sup> with cyclopentadiene synthetically useful<sup>4</sup> bicyclo[3.2.0]hept-2-en-6ones are formed (eq 1) with remarkable stereoselectivity. 6 These

$$\begin{array}{c} L \\ S \\ \end{array} C = C = 0 + \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\$$

cycloadditions are always highly periselective<sup>3,7</sup> (only (2 + 2) and no (4 + 2) for all-carbon ketenophiles), supraselective<sup>8</sup> on the diene (only cis-fused products), regioselective<sup>8,9</sup> (no bicyclo[3.2.0]-hept-2-en-7-ones), and somewhat less highly spatioselective<sup>10-12</sup> (when  $L \neq S$  the larger ketene substituent L prefers the more hindered endo position). These unusual stereochemical features are consistent with an allowed  $(\pi^2 + \pi^2)$  process in which the ketene acts antarafacially, and the reaction has been widely interpreted as concerted. 13-15

Symmetry"; Verlag Chemie: Weinheim, 1970.

<sup>(9)</sup> R. A. Mackay, K. Letts, and C. Jones, "Micellization, Solubilization and Microemulsions", Vol. 2, Mittal K. L., Ed., Plenum Press, New York,

<sup>1977,</sup> p 801.
(10) C. E. Jones and R. A. Mackay, "Porphyrin Chemistry Advances", F.

<sup>R. Longo, Ed., Ann Arbor Science, Ann Arbor, MI, 1979, p 71.
(11) K. Kalyanasundaram and J. K. Thomas, J. Am. Chem. Soc., 99, 2039</sup> 

<sup>(12)</sup> M. Almgren, F. Grieser, and J. K. Thomas, J. Am. Chem. Soc., 102, 3188 (1980).

<sup>(1)</sup> For part 1 see: Holder, R. W.; Daub, J. P.; Baker, W. E.; Gilbert, R. H., III; Graf, N. A. J. Org. Chem. 1982, 47, 1445.

<sup>(2)</sup> In part abstracted from Graf, N. A. B.S. Thesis, University of New

<sup>(3)</sup> Staudinger, H. "Die Ketene"; Enke: Stuttgart, 1912.

<sup>(4)</sup> Brady, W. T. In "The Chemistry of Ketenes, Allenes, and Related Compounds"; S. Patei, Ed.; Wiley: New York, 1980; Part 1, Chapter 8.

(5) Ulrich, H. "Cycloaddition Reactions of Heterocumulenes"; Academic

<sup>(9)</sup> Ghozer, L.; Montaigne, R.; Moller, P. Teridding, A. S. Helly, Chim. B. Chim. Chim. B. Chim. B. Chim. Chim. Chim. B. Chim. Chim. Chim. Chim. Chim. B. Chim. (10) Rey, M.; Roberts, S.; Dieffenbacher, A.; Dreiding, A. S. Helv. Chim. Acta 1970, 53, 417.

<sup>(11)</sup> Brady, W. T.; Roe, R. R., Jr. J. Am. Chem. Soc. 1970, 92, 4618.

<sup>(12)</sup> Brady, W. T.; Roe, R. R., Jr. J. Am. Chem. Soc. 1971, 93, 1662.
(13) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital

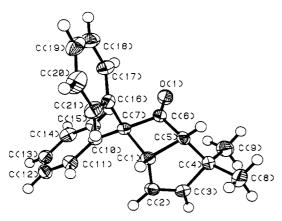


Figure 1. ORTEP diagram (30% ellipsoids) of 3 with hydrogen atoms shown as spheres of radius 0.2 Å. The regiochemistry is indicated by the bond lengths of  $C_2$ - $C_3$  and  $C_3$ - $C_4$  (1.304 and 1.518 Å, respectively).

Scheme Ia

<sup>a</sup> (a) 80 °C benzene solution; (b) X = D, Y = H; (c) X = H, Y = D.

Nevertheless, a secondary deuterium kinetic isotope effect (2°D KIE) study of the reaction of cyclohexene-1- $d_1$  and diphenylketene (1) showed the transition state to be at least asymmetric. 16 The KIE technique<sup>17,18</sup> for measuring the synchrony of new bond formations<sup>19</sup> was subsequently applied to the cycloaddition of styrene and 1,<sup>20,21</sup> and the results, although somewhat anomalous,<sup>22</sup> interpreted in favor of a concerted process. We now report our study of the reaction of 5,5-dimethylcyclopentadiene (2)25 and 1, for which the 2°D KIE's indicate a nonconcerted mechanism.

In spite of the methyls, the reaction takes the ordinary course (eq 2). Refluxing 0.49 g of  $1^{27}$  and 0.25 g of  $2^{1}$  in 10 mL of

$$Ph_{2}C=C=0 + 4 \underbrace{\begin{array}{c} CH_{3} & CH_{3} \\ 5 & \end{array}}_{2} \xrightarrow{\begin{array}{c} CH_{3} \\ 4 & \end{array}}_{2} \xrightarrow{\begin{array}{c} CH_{3} \\ 6 & \end{array}}_{1} (2)$$

- (14) Dewar, M. J. S. Angew. Chem., Int. Ed. Engl. 1971, 10, 761.
- (15) Zimmerman, H. E. Acc. Chem. Res. 1971, 4, 272.
  (16) Katz, T. J.; Dessau, R. J. Am. Chem. Soc. 1963, 85, 2172.
- (17) Melander, L. "Isotope Effects on Reaction Rates"; Ronald Press:
- (17) Melandel, L. Isotope Effects on Reaction Rates, Rohald Pless. New York, 1960.
  (18) "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowmann, N. S., Eds.; ACS Monograph 167; Van Nostrand-Reinhold: New York, 1970.
  (19) Dolbier, W. R. In "Isotopes in Organic Chemistry"; Buncel, E., Lee, C. C., Eds.; Elsevier: Amsterdam, 1975; Vol. 1, Chapter 2.
  (20) Baldwin, J. E.; Kapecki, J. A. J. Am. Chem. Soc. 1970, 92, 4874.
- (21) Collins, C. J.; Benjamin, B. M.; Kabalka, G. W. J. Am. Chem. Soc. 1978, 100, 2570.
- (22) One new bond, corresponding to  $C_5$ – $C_6$  in eq 1, showed an inverse 2°D KIE  $(k_H/k_D = 0.91)$  as expected 19,23,24 for an sp<sup>2</sup>  $\rightarrow$  sp<sup>3</sup> rehybridization in the slow step. The other new bond, corresponding to  $C_1$ – $C_7$  in eq 1, showed a large normal effect  $(k_H/k_D = 1.23)$ , which was interpreted as due to a unique type of hypersonium ties. unique type of hyperconjugation.
- (23) Streitwieser, A., Jr.; Jagow, R. H.; Fahey, R. C.; Suzuki, S. J. Am. Chem. Soc. 1958, 80, 2326.
- (24) Wolfsberg, M.; Stern, M. J. Pure Appl. Chem. 1964, 8, 225, 325; J. Chem. Phys. 1966, 45, 2618.
- (25) It would be extremely difficult to carry out our experiment with deuterium-labeled cyclopentadiene itself since facile [1,5] hydrogen sigmatropic shifts<sup>26</sup> would rapidly scramble the label.

Table I. Ratios of Integrated Areas of Adduct 3 Prepared from Deuterated 5,5-Dimethylcyclopentadienes

starting diene	ratio of integrated areas <sup>a</sup>					
	$H_1/H_2$	H <sub>s</sub> /H <sub>3</sub>	$D_2/D_3$	$D_3/D_5$		
2-1-d,	$0.99 \pm 0.01$	$0.84 \pm 0.02^{b}$		0.82 <sup>b</sup>		
<b>2-2-</b> d	$0.98 \pm 0.02^{c}$	$1.00 \pm 0.01$	1.06 <sup>c</sup>			

<sup>a</sup> Proton ratios are the average of at least four separate integrations carried out on a 220-MHz continuous wave instrument. Errors are  $2\sigma$ . Deuterium ratios are the results of single experiments carried out on a 360-MHz Fourier transform instrument.  $^b$  The 2°D KIE for  $C_s$ - $C_6$  bond formation.  $^c$  The 2°D KIE for  $C_1$ - $C_7$  bond for-

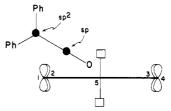


Figure 2. Suggested approach of diphenylketene to 5,5-dimethylcyclopentadiene.  $\square$  represents a methyl group. The ketene p orbitals that form the new bonds are shown as filled circles. The orthogonal p orbitals of the carbonyl bond are omitted for clarity. Eventual bonding will be between C<sub>1</sub> and the sp carbon and between C<sub>2</sub> and the sp<sup>2</sup> carbon bearing the two phenyls.

benzene affords 96% 4,4-dimethyl-7,7-diphenylbicyclo[3.2.0]hept-2-en-6-one (3), after concentration and recrystallization (ethanol), as white crystals, mp 149-150 °C. The spectral features<sup>28</sup> and combustion analysis<sup>29</sup> are consistent with the expected structure but insufficient to assign the regiochemistry. Accordingly, an X-ray crystallographic study was performed that confirms (Figure 1) the assigned structure 3 in every detail.

Since our preliminary kinetic studies<sup>30</sup> show only a minimal rate difference (cyclopentadiene reacts about 10 times faster than 2 under pseudo-first-order conditions) and since the reaction shows the normal stereoselectivity (in those three modes possible for a symmetrical ketene), we conclude the gem-methyl substitution does not appreciably alter the course of the reaction.

Simple modifications of our route<sup>1</sup> provide 2 deuterated at C<sub>1</sub>  $(2-1-d_1)$  and, separately, at  $C_2$   $(2-2-d_1)$ . In each case, <sup>1</sup>H and <sup>13</sup>C NMR confirm the isotope location and content as  $\geq 98\% d_1$ . Reaction of 1 with  $2-l-d_1$  affords 5a + 5b, and with  $2-2-d_1$  mixture 6a + 6b is formed (Scheme I). We define the intramolecular 2°D KIE for C<sub>5</sub>-C<sub>6</sub> bond formation as  $k_{\rm H}/k_{\rm D} = 5a/5b$ , and that for  $C_1$ - $C_7$  bond formation as  $k_H/k_D = 6a/6b$ . Table I presents the data, obtained from both  $^1H$  and  $^2H$  NMR of adduct mixtures 5 and 6.

Since the 2°D KIE observed for 2-1- $d_1$  is large and inverse, it is evident 19,23,24 that there is extensive sp<sup>2</sup>  $\rightarrow$  sp<sup>3</sup> rehybridization of C<sub>1</sub> of the diene in the rate-determining step. The 2°D KIE observed for  $2-2-d_1$ , however, is essentially unity, consistent with no rehybridization occuring at C2 of the diene during the slow step.<sup>31</sup> In order to account for the periselectivity as well as the 2°D KIE's, we suggest the ketene approaches the diene in the orthogonal manner (see Figure 2 of ref 6) usually assumed, but

(26) Berson, J. A.; Aspelin, G. G. Tetrahedron. 1964, 20, 2697

(26) Berson, J. A.; Aspeiin, G. G. Tetranearon. 1964, 20, 2697.

(27) Hawks, G. W.; Mckillop, A.; Taylor, E. C. Org. Synth. 1972, 52, 36.

(28) IR (CHCl<sub>3</sub>) 1770, 1601 cm<sup>-1</sup>; <sup>1</sup>H NMR (80 Mhz, CDCl<sub>3</sub>) δ 7.5–7.0

(m, 10 H), 5.55 (m, 1 H (H<sub>3</sub>)), 5.35 (m, 1 H (H<sub>2</sub>)), 4.35 (m, 1 H (H<sub>1</sub>)), 3.45

(m, 1 H (H<sub>3</sub>)), 1.30 (s, 3 H), 1.05 (s, 3 H); <sup>13</sup>C[H] NMR (20 Mhz, CDCl<sub>3</sub>) δ 210.37, 144.76, 141.39, 140.53, 128.61, 128.07, 127.62, 127.23, 127.09, 126.94, 126.34, 79.07, 68.67, 49.10, 48.45, 30.22, 24.06.

(29) Anal. Calcd for  $C_{21}H_{20}O$ : C, 87.46; H, 6.99. Found: C, 87.40; H, 7.07. We thank Ruby Ju of our department for this analysis.

(30) Carried out in a manner similar to that of Huisgen et al.: Huisgen, R.; Feiler, L. A.; Otto, P. Chem. Ber. 1969, 102, 3444.
(31) Pryor<sup>32</sup> has shown that the 2°D KIE for an sp<sup>2</sup> (double bond) → sp<sup>2</sup>

(radical center) change to be near 1.03.
(32) Henderson, R. W.; Pryor, W. A. Int. J. Chem. Kinet. 1972, 4, 325.

with the carbon bearing the bulky phenyls canted considerably farther away from the diene (Figure 2). At the rate-determining transition state there is then considerable bonding between  $C_1$  of the diene and the sp carbon of 1 but essentially none between  $C_2$  of the diene and the sp<sup>2</sup> carbon of 1.

Nevertheless, in the subsequent step, and because of the original approach geometry, the ketene's  $sp^2$  carbon finds itself closer to  $C_2$  of the diene than to  $C_4$ , and thus the intermediate<sup>33</sup> closes to give only the (2 + 2) product.

If this picture is correct, it not only illustrates the power of isotope effect studies to help determine the structures of transition states but suggests that less bulky substituents on the ketene may lead to some bonding at both  $C_1$  and  $C_2$  of the diene (and hence to inverse 2°D KIE's at both positions) as the cycloaddition is

sterically allowed to become concerted (but not necessarily synchronous). Studies designed to test this hypothesis are underway, but some support is already available from the work of Isaacs, 35 who found a substantial *inverse* 2°D KIE at the  $\alpha$ -carbon of styrene reacting with dimethylketene, in contrast to the large *normal* effect at the same position when styrene reacts with 1.<sup>20</sup>

Acknowledgment. We are grateful to Professor J. J. Gajewski, Indiana University, for the NMR measurements and a helpful discussion and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Supplementary Material Available: Crystal and data collection parameters, final positional and thermal parameters, bond lengths and angles, torsion angles, and observed and calculated structure amplitudes (11 pages). Ordering information is given on any current masthead page.

## Book Reviews

Heterocyclic Chemistry. Volume 1. Senior Reporters: H. Suschitzky and O. Meth-Cohn. The Royal Society of Chemistry, London. 1980. 522 pp. £69.00; \$194.50.

This new member of the Specialist Periodical Report series contains a combination of the type of material previously reviewed in other volumes in the series, namely "Saturated Heterocyclic Chemistry", "Aromatic and Heteroaromatic Chemistry" (both of which are now discontinued), and the heterocyclic portion of "Organic Compounds of Sulphur, Selenium, and Tellurium" (which will still continue to report on  $\beta$ -lactam antibiotic chemistry).

The reporters state that the literature covered is essentially based in volumes 89 and 90 of "Chemical Abstracts", i.e., July 1978 to June 1979, with some later papers included to provide continuity.

The style and format follow those of the revered "Annual Reports of the Chemical Society", providing almost encyclopaedic coverage of the subject (with some notable exceptions, vide infra) for the period. Syntheses and/or reactions are mentioned very briefly, an equation or a structure may be given, the occasional mechanism outlined, and the appropriate literature reference given (occasionally, reference is made to another Specialist Periodical Report rather than to the original article: this makes it difficult for the reader to check since the paper may well be available while the Report may not).

The format is traditional, with small rings being treated first, going from small to large rings, and giving preference to the smaller heterocycle in fused systems. In addition, articles on "Bridged Systems" and on "Conformational Analysis" are included because of their relevance to saturated heterocycles. References to reviews published during the period are given at the beginning of each chapter. The chapters (and reporters) are: 1. Three-membered Ring Systems (T. J. Mason). 2. Four-membered Ring Systems (R. C. Storr). 3. Five-membered Ring Systems (Thiophens, and their Selenium and Tellurium Analogues by S. Gronowitz; Systems Containing Nitrogen and Sulphur, Selenium, or Tellurium, by P. A. Lowe; Other Five-membered Ring Systems, by G. V. Boyd). 4. Six-membered Ring Systems (Azines, Oxazines, and Thiazines, by R. K. Smalley; other Six-membered Ring Systems, by G. P. Ellis). 5. Seven-membered Ring Systems (D. J. LeCount). 6. Eightmembered and Larger Ring Systems (including macrocycles) (G. M. Brooke). 7. Bridged Systems (J. M. Mellor). 8. Conformational Analysis (F. G. Riddell).

The treatment is purely descriptive and uncritical (and is meant to be so). As might be expected in a review as extensive as this one, many errors creep into it. For example, a  $CH_2$  is missing from structure 73 (p 14); an extra methyl group is present in 115 (p 19) and the need for a lithiating agent is not mentioned; formation of diazolidines (760) (p 234) requires the use of aroyl isothiocyanates; in 878 (p 244), R = H only, and a hydrogen is missing on the nitrogen of 879; a methyl group

is missing in 43 (p 339) and a double bond in the ring at the bottom of that page; the dichloronorcaranes on p 331 are really dichloro-2-oxanorcaranes; on p 115, it is the N-(chlorothio)-1,2-benzisothiazol-3-one 1,1-dioxides that undergo reaction with arenethiols and not the N-chloro compounds; in the product (34) R = ArS, not R = Ar; methyl groups are missing in 880 and 881 on p 244, but are present (as required) in Scheme 28 (p 282) where the same reaction is discussed again. There are also a number of misstatements, e.g., p 26, Direct Insertion rather than Direct Addition; p 28, indole N-oxide rather than (3H)-indole (or indolenine) N-oxide; bicyclo-derivatives 81 (p 276) are classified as dihydropyridines; on p 337 it is stated that substituents or hydrogen in pyrylium salts are susceptible to nucleophilic displacement, but no example of this is given—instead the addition of methoxide ion is referred to. Such errors are almost inevitable in such an extensive, broad-ranging treatment. Many will stimulate the curiosity of the reader (as they did this reviewer) and send him to the literature for an explanation. Many unusual transformations are mentioned but not explained—once again, a trip to the library is thereby encouraged!

In spite of the very extensive coverage, much had to be left out to maintain the chapters to a "prescribed length", e.g., much of the patent literature on 1,4-benzodiazepines and tricyclic antidepressants, about one third of the articles on Other Five-membered Ring Systems. Virtually no mention is made of any biological activity in the compounds. This brings up an important point regarding such Specialist Reports. In spite of their covering a great deal of the literature on a given topic, they are not-and probably cannot be-exhaustive in their coverage and the reader will have to go to the original sources for a complete literature search. Presumably, then, the reports will be of use to heterocyclic chemists who will leaf through them in search of inspiration or look at them more carefully for leading references, realizing they may be missing something important to their research work. Certainly, the format does not make for casual reading! Indeed, one has to be either very dedicated or a reviewer to read more than a few pages in detail at one sitting! The very high price of the volume almost surely ensures that most heterocyclic chemists will not be able to afford their own copy-even some large university libraries may have a difficult time justifying the expense, particularly when the research chemist will have to go to the primary literature anyway to get all the information he wants and needs.

The senior reporters and reporters have done a monumental job with this compilation and, overall, have done it very well. This reviewer feels that a copy should be available in all research libraries that can afford it so that students and researchers can browse through it and see the many things they themselves have missed in their own general survey of the literature of heterocyclic chemistry, and occasionally find inspiration (as this reviewer did more than once) in a reaction or structure. It is no substitute—and was obviously not meant to be—for a thorough literature search of areas of immediate concern.

<sup>(33)</sup> Our present information is insufficient to describe the intermediate as either a diradical or a zwitterion, although it is interesting that a (2 + 2) cycloaddition known to traverse a dipolar intermediate shows one 2°D KIE as inverse and the other as normal.<sup>34</sup>

<sup>(34)</sup> von Gustorf, E. K.; White, D. V.; Leitich, J.; Henneberg, D. Tetrahedron Lett. 1969, 3113.

<sup>(35)</sup> Isaacs, N. S.; Hatcher, B. G. J. Chem. Soc., Chem. Commun. 1974,