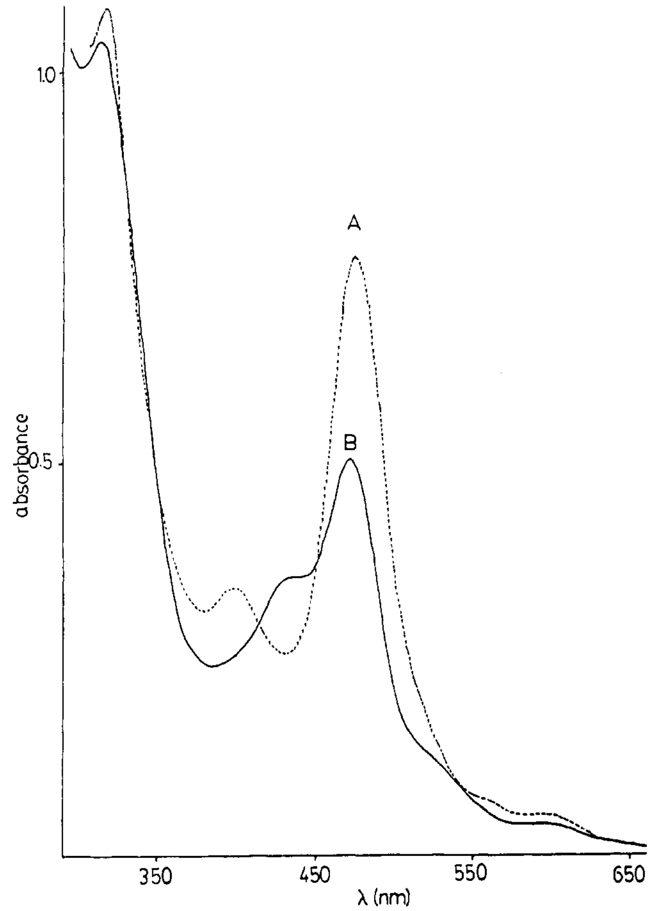


Figure 4. The visible spectra of $(Ph_4P)_2[(FeCl_2)_2MoS_4]^{2-}$ in the same concentration (9×10^{-4} M) in (A) CH_2Cl_2 and (B) DMF.

ligand than as a terminal bidentate chelate in III or IV is found in the solution behavior of I.

The visible spectrum of I varies with the polarity of the solvent, and spectra obtained in DMF [600 nm (sh), 522 (sh), 472 (ϵ 5849), 432 (4070), 314 (12 250)] are different from those obtained in CH_2Cl_2 [600 nm (ϵ 580), 566 (sh), 475 (9892), 398 (4369), 319 (13 870)] (Figure 4). Following the addition of 1 equiv of MoS_4^{2-}, the spectrum of I in CH_2Cl_2 changes and becomes virtually identical with that obtained in DMF. Alternatively, the visible spectrum of I in DMF and in the presence of an excess of anhydrous $FeCl_2$ is very similar to that obtained for I alone in CH_2Cl_2.

These observations suggest that, in polar solvents, I dissociates according to the equilibrium $[Cl_2FeS_2MoS_2FeCl_2]^{2-} \rightleftarrows [Cl_2FeS_2MoS_2]^{2-} + FeCl_2$. The same behavior is found with the tungsten analogue (II) for which the spectra are as follows: in CH_2Cl_2, 502 nm (ϵ 930), 418 (7100), 360 (5400), 294 (14 200); in DMF, 524 nm (ϵ 530), 417 (6300), 373 (7110). The $(Ph_4P)_2[Cl_2FeS_2MS_2]$ complexes (M = Mo, brown-red crystals; M = W, red orange crystals, V and VI, respectively) form by the reactions I or II with equimolar amounts of $(Ph_4P)_2MoS_4$ or $(Ph_4P)_2WS_4$ in DMF. They are isolated in crystalline form, and in excellent yields, upon the addition of ether to the DMF solutions.[16]

In conclusion, the structure of I demonstrates for the first time the ability of MoS_4^{2-} to serve as a doubly bridging ligand.[17] Clearly, the Mo-S bond lengths in I are shorter than those reported for the Mo site in nitrogenase which probably contains Mo in a lower formal oxidation state. In its entirety, I cannot be considered as a model; however, it contains gross structural features in common with one of the minimal models (Figure 1, **B**) proposed for the Mo site in nitrogenase on the basis of the EXAFS studies. At present we are investigating the coordination chemistry of the bridging MoS_4^{2-} ligand.

Acknowledgments. This work has been supported by grants from the National Science Foundation (CHE-79-0389), the National Institutes of Health (GM 26671-01), and a NATO Research Grant No. (1321).

Supplementary Material Available: Structure factors and positional coordinates for $(Ph_4P)_2[Cl_2FeS_2MoS_2FeCl_2]$ (27 pages). Ordering information is given on any current masthead page.

References and Notes

(1) D. Coucouvanis, N. C. Baenziger, E. D. Simhon, P. Stremple, D. Swenson, A. Kostikas, A. Simopoulos, V. Petrouleas, and V. Papaefthymiou, *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) S. P. Cramer, K. O. Hodgson, W. O. Gillum, and L. E. Mortenson, *J. Am. Chem. Soc.*, **100**, 3398 (1978).
(3) T. E. Wolff, J. M. Berg, K. O. Hodgson, R. B. Frankel, and R. H. Holm, *J. Am. Chem. Soc.*, **101**, 4140 (1979).
(4) D. Coucouvanis, E. D. Simhon, D. Swenson, and N. C. Baenziger, *J. Chem. Soc., Chem. Commun.*, 361 (1979).
(5) A. Kostikas, V. Petrouleas, A. Simopoulos, D. Coucouvanis, and D. G. Holah, *Chem. Phys. Lett.*, **38**, 582 (1976).
(6) P. G. Debrunner, E. Münck, L. Que, and C. E. Schulz in "Iron-Sulfur Proteins", Vol. III, W. Lovenberg, Ed., Academic Press, New York, 1977, Chapter 10 and references therein.
(7) For the reported mean values, the larger of the standard deviations from the mean $(\sum_{i=1}^{N}[(\chi_i - \bar{\chi})^2/(N-1)]^{1/2})$ or the standard deviations (as derived from the inverse matrix) are reported.
(8) Trinh-Toan and L. F. Dahl, *J. Am. Chem. Soc.*, **93**, 2654 (1971).
(9) J. W. Lauher and J. A. Ibers, *Inorg. Chem.*, **14**, 348 (1975).
(10) T. J. Kistenmacher and G. D. Stucky, *Inorg. Chem.*, **7**, 2150 (1968).
(11) F. A. Cotton and C. A. Murrillo, *Inorg. Chem.*, **14**, 2467 (1975).
(12) M. A. Bobrik, K. O. Hodgson and R. H. Holm, *Inorg. Chem.*, **16**, 1851 (1977).
(13) D. Coucouvanis, D. Swenson, P. Stremple, and N. C. Baenziger, *J. Am. Chem. Soc.*, **101**, 3392 (1979).
(14) J. J. Mayerle, S. E. Denmark, B. V. DePamphilis, J. A. Ibers, and R. H. Holm, *J. Am. Chem. Soc.*, **97**, 1032 (1975).
(15) The ability of the terminal ligands to undergo this change may well affect the ease by which the Fe–L bridge can be lengthened. Such lengthening is expected to occur on reduction of the Fe(III)-containing dimers, $[Fe_2S_2L_4]^{2-}$.
(16) The $[Cl_2FeS_2MoS_2]^{2-}$ complex anion has been synthesized via an alternate route and the crystal and molecular structures of the Et_4N^+ salt of this complex have been determined: B. Averill and B. Teo, private communication.
(17) A triply bridging MoS_4^{2-} unit has been observed recently in the structure of the very interesting $[Mo_2S_8Ag_4](PPh_3)_4$ molecule: A. Müller, H. Bögge, E. Königer-Ahlborn, and W. Hellman, *Inorg. Chem.*, **18**, 2301 (1979).

D. Coucouvanis,* N. C. Baenziger
E. D. Simhon, P. Stremple, D. Swenson
Department of Chemistry, University of Iowa
Iowa City, Iowa 52242

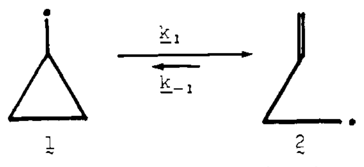
A. Simopoulos, A. Kostikas
V. Petrouleas, V. Papaefthymiou
Nuclear Research Center, "Demokritos"
Aghia Paraskevi, Attiki, Greece

Received October 29, 1979

Allylcarbinyl–Cyclopropylcarbinyl Rearrangement[1]

Sir:

The *ring opening* of cyclopropylcarbinyl (**1**) to the 3-butenyl radical (**2**) has been extensively investigated in recent years, as have a number of related reactions.[2] This reaction is extremely rapid but its rate has, nevertheless, been measured by kinetic EPR spectroscopy.[3] The Arrhenius equation for ring opening was found to be[3,4]



0002-7863/80/1502-1734$01.00/0

Table I. EPR Data and Calculated Rate Constants[a]

run	T, °C	[**4**] × 10^7	[**5**] × 10^7	$(k_{-1}/2k^{55}) \times 10^7$	$2k^{55} \times 10^{-9}$ [b]	k_{-1}
A	−21.0	4.62	0.51	1.27	2.79	354
B	−17.5	3.49[c]	0.48[c]	1.27	2.98	378
B	−16.5	3.54[d]	0.48[d]	1.26	3.04	383
A	−11.0	3.64	0.76	2.32	3.35	777
A	−9.5	4.55[e]	0.93[e]	2.82	3.44	970
B	−4.5	3.38[d]	0.76[d]	2.40	3.74	898
B	−3.5	3.43	0.76	2.39	3.81	911
B	0	3.20	0.74	2.37	4.03	955
B	3.5	2.35	0.78	3.11	4.26	1325

[a] Concentrations are in moles/liter, rate constants in mole, liter, second units. [b] Calculated from data in ref 23b and 23c for a solvent 17% more viscous than *n*-octane. [c] Average of four separate measurements. [d] Average of three separate measurements. [e] Average of two separate measurements.

$$\log (2k_1/\mathrm{s}^{-1}) = (12.48 \pm 0.85) - (5.94 \pm 0.57)/\theta \quad (1)$$

where $\theta = 2.3\,RT$ kcal/mol. At 25 °C this equation gives $2k_1 = 1.3 \times 10^8\ \mathrm{s}^{-1}$. Labeling experiments of various kinds have shown, via the scrambling of the label, that the reverse reaction *can* occur.[2,5] However, there has been, to date, no *experimental* determination of the rate constant for ring closing, k_{-1}. The equilibrium constant for this intriguing rearrangement has not been determined either indirectly ($K = k_1/k_{-1}$) or directly. It has had to be estimated[6] from "appropriate"[7] thermochemical quantities. The enthalpy change for this equilibrium has also been computed by ab initio[8] and by MINDO/3[9,10] methods. We have now measured k_{-1} by two different experimental techniques at temperatures from −21 to 80 °C. To the best of our knowledge, the present work represents the first determination of the equilibrium constant for a radical rearrangement which involves a substantial change in structure.

Technique 1. 1-Bromo-1,1-dideuteriobut-3-ene (**3**) was reacted in benzene under the usual free-radical conditions[11] with tri-*n*-butyltin hydride and the yields of the two deuterated butene products, **6** and **7**, were monitored by ^{2}H NMR. The rate constant for the reaction of a primary alkyl with *n*-Bu$_3$SnH has been measured at 25 °C[12] and the Arrhenius parameters for this reaction have been estimated[13] to be E = 3.1 kcal/mol, $\log (A/\mathrm{M}^{-1}\,\mathrm{s}^{-1}) = 8.3$. Experiments at 40, 60, and 80 °C, yielded the following values for k_{-1}:[16] 9.4×10^3, 2.6×10^4, and $6.2 \times 10^4\ \mathrm{s}^{-1}$, respectively.

$$\underset{\mathbf{3}}{\mathrm{CH_2{=}CHCH_2CD_2Br}} + n\text{-}\mathrm{Bu_3Sn\cdot} \rightarrow \underset{\mathbf{4}}{\mathrm{CH_2{=}CHCH_2CD_2\cdot}} + n\text{-}\mathrm{Bu_3SnBr}$$

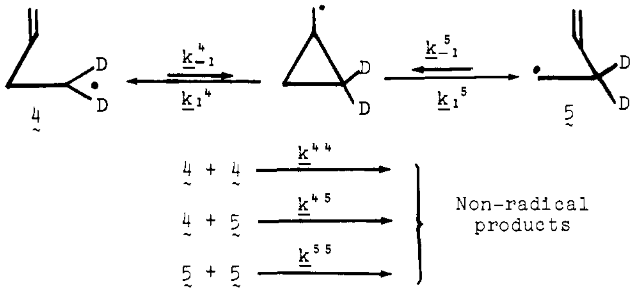
$$\mathrm{CH_2{=}CHCH_2CD_2\cdot} \underset{\circ}{\rightleftharpoons} [\dot{\mathrm{C}}\mathrm{H_2}\overline{\mathrm{CHCH_2C}}\mathrm{D_2}] \underset{\circ}{\rightleftharpoons} \mathrm{CH_2{=}CHCD_2CH_2\cdot}$$

$$\mathrm{CH_2{=}CHCH_2CD_2\cdot} + n\text{-}\mathrm{Bu_3SnH} \xrightarrow{k_\mathrm{H}} \underset{\mathbf{6}}{\mathrm{CH_2{=}CHCH_2CD_2H}} + n\text{-}\mathrm{Bu_3Sn\cdot}$$

$$\mathrm{CH_2{=}CHCD_2CH_2\cdot} + n\text{-}\mathrm{Bu_3SnH} \xrightarrow{k_\mathrm{H}} \underset{\mathbf{7}}{\mathrm{CH_2{=}CHCD_2CH_3}} + n\text{-}\mathrm{Bu_3Sn\cdot}$$

Technique 2. 1,1-Dideuterio-3-butenyl (**4**) was generated directly in the cavity of a Varian E-104 EPR spectrometer by photolysis of the corresponding diacyl peroxide[17] and by photolysis of hexamethylditin (10% v/v), di-*tert*-butyl peroxide (15% v/v), and **3** (0.1 M), in isooctane.[18,19] At temperatures below ca. −40 °C only **4** was observed, but at higher temperatures **5** was also present.[20] The cyclopropylcarbinyl radical was not observed at any temperature. The overall reaction can be represented as shown in Scheme I. The ring-opening reaction is expected to exhibit a small, normal, secondary deuterium isotope effect (i.e., $k_1^5/k_1^4 > 1.0$) and the ring closure an inverse isotope effect of similar magnitude.[22] Putting $k_1^5/k_1^4 = k_{-1}^4/k_{-1}^5 = \alpha$, and assuming that the bimolecular radical-radical reactions are diffusion controlled[23] (which means that $2k^{44} = k^{45} = 2k^{55}$), then, under steady-state conditions and with the partially equilibrated system being populated via **4**, the following equation can be derived:

Scheme I



$$\frac{k_{-1}^5}{2k^{55}} = \frac{(1+\alpha)[\mathbf{5}]([\mathbf{4}]+[\mathbf{5}])}{\alpha^2[\mathbf{4}] - [\mathbf{5}]} \quad (2)$$

Thus, $k_{-1}^5/2k^{55}$ should be obtainable by measurement of the absolute concentrations of **4** and **5** (via double integration of nonoverlapping lines in their spectra) at temperatures below those where complete equilibration occurs provided that α is either known or is close to 1.0. This simple idea represents a new kinetic application of EPR spectroscopy.

Experimentally the bromide/ditin system was found to give somewhat better spectra than the diacyl peroxide. Absolute radical concentrations were measured in the former system in two quite separate experiments (A and B) over a range of temperatures from 3.5 to −21.0 °C (see Table I). The value of α is unknown but it is highly unlikely to be greater than 1.2 or 1.3.[22] We have therefore calculated k_{-1}^5, which is presumably equal to k_{-1}, on the assumption that $\alpha = 1.0$. If α were as large as 1.3 the values of $k_{-1}/2k^{55}$ and k_{-1} in Table I would have to be reduced by ~40%. Values of $2k^{55}$ were calculated from Schuh and Fischer's[23b,c] extremely accurate data on the diffusion-controlled bimolecular self-reaction of *tert*-butyl[24] using a solvent viscosity equal to that measured for our reaction medium[25] (see Table I). An Arrhenius plot of the k_{-1} values obtained by both technique 1 and 2 is shown in Figure 1. It is clear that the two sets of data are in satisfactory agreement. This gives us renewed confidence in the validity of both experimental techniques and in the potential usefulness of eq 2.

The data summarized in Figure 1 can be represented by

$$\log (k_{-1}/\mathrm{s}^{-1}) = (10.3_6 \pm 0.5) - (9.0_9 \pm 0.5)/\theta \quad (3)$$

with the estimated error limits taking the uncertain value of α into account. Combining a statistically corrected eq 1 with eq 3 yields

$$\log K = \log (k_1/k_{-1}) = 1.82 + 3.15/\theta$$
$$\text{i.e., } K = 1.3 \times 10^4 \text{ at } 25\ ^\circ\mathrm{C} \quad (4)$$

Table II. Thermochemistry. Comparison of Experiment with Theory

E_{-1}[a]	$\log (A_{-1}/s^{-1})$	$-\Delta H°$ [a]	$\Delta S°$ [b]	ref
9.09	10.36	3.15	8.3 (9.7)[c]	this work
		5.2	6.6	6
17.3		8.6		8
12.4	11.46	0.25	7.2	9
12.9		0.5		10

[a] In kilocalories/mole. [b] In calories/mole K. [c] Statistically corrected. It is not clear whether the other $\Delta S°$ values have or have not been corrected.

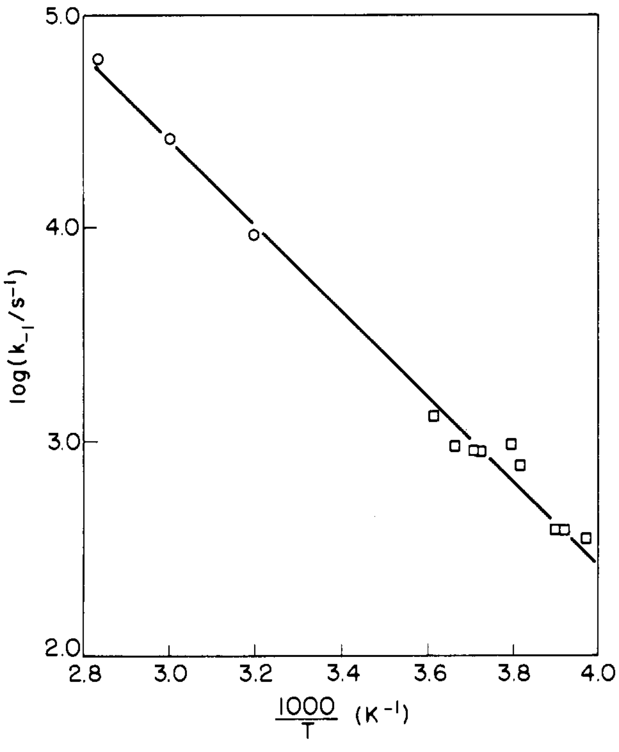


Figure 1. Plot of $\log (k_{-1}/s^{-1})$ against $1/T$: ○, technique 1; □, technique 2.

The relative concentrations of **1** and **2** under equilibrium conditions must be calculated from the relation

$$\log K' = \log (2k_1/k_{-1}) = 2.12 + 3.15/\theta$$
$$K' = 2.6 \times 10^4 \text{ at } 25\ °C \quad (5)$$

Our present experimental results are compared in Table II with thermochemical quantities that have been previously estimated or calculated.

Finally, we estimate that line broadening in the EPR spectrum of the unlabeled 3-butenyl radical resulting from rapid exchange of the α and β hydrogens should occur at a temperature of ~400 °C. Unfortunately, EPR experiments at such elevated temperatures, though possible,[26] are not easy to carry out.

Acknowledgment. We thank Professor J. Warkentin and an unnamed referee for some extremely valuable comments on this work.

References and Notes

(1) Issued as N.R.C.C. No. 18092.
(2) For reviews see: Wilt, J. W. In "Free Radicals", Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 8. Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States", de Mayo, P., Ed.; Academic: New York, in press. See also Castaing, M.; Pereyre, M.; Ratier, M.; Blum, P. M.; Davies, A. G. *J. Chem. Soc., Perkin Trans. 2* **1979**, 287, and references cited therein.
(3) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024.
(4) A statistical factor of 2 has been introduced because either of two equivalent bonds in the ring may cleave.
(5) Montgomery, L. K.; Matt, J. W. *J. Am. Chem. Soc.* **1967**, *89*, 3050, 6556.
(6) Carter, W. P. L.; Tardy, D. C. *J. Phys. Chem.* **1974**, *78*, 1245.
(7) Obtained[6] from the following sources: O'Neal, H. E.; Benson, S. W. *Int. J. Chem. Kin.* **1969**, *1*, 221. Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279. McMillen, D. F.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kin.* **1971**, *3*, 359.
(8) Hehre, W. J. *J. Am. Chem. Soc.* **1973**, *95*, 2643.
(9) Bischof, P. *Tetrahedron Lett.* **1979**, 1291.
(10) Dewar, M. J. S.; Olivella, S. *J. Am. Chem. Soc.* **1979**, *101*, 4958.
(11) Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1726.
(12) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047.
(13) Obtained by combining kinetic data for the cyclization of the 5-hexenyl radical[14] with the results of a product study on the reaction of 5-hexenyl with tri-*n*-butyltin hydride.[15]
(14) Schmid, P.; Griller, D.; Ingold, K. U. *Int. J. Chem. Kin.* **1979**, *11*, 333.
(15) Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Chem. Commun.* **1974**, 472, and further unpublished results.
(16) Calculated from the integrated rate expression

$$[\mathbf{7}]_f = \frac{k_1}{2k_H}\left\{\frac{[Bu_3SnH]_i + (k_{-1}/k_H)}{[Bu_3SnH]_f + (k_{-1}/k_H)}\right\}$$

where the subscripts i and f refer to initial and final concentrations. Values of k_{-1} are averages of 6, 10, and 16 determinations at 40, 60, and 80 °C, respectively. The tin hydride was normally consumed completely. Three typical experiments at 80 °C follow: $[Bu_2SnH]_i = 0.202, 0.125$, and 0.077 M which gave $[\mathbf{7}]_f = 0.0270, 0.0232$, and 0.0175 M, respectively. Taking $k_H = 2.4 \times 10^6\ M^{-1}\ s^{-1}$, these experiments yield $k_{-1} = 5.8, 6.5$, and $6.0 \times 10^4\ s^{-1}$.
(17) Kochi, J. K.; Krusic, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 3940. Sheldon, R. A.; Kochi, J. K. *Ibid.* **1970**, *92*, 4395.
(18) Griller, D. *Magn. Reson. Rev.* **1979**, *5*, 1.
(19) With hexa-*n*-butylditin the desired radical, **4**, was produced, but it was "contaminated" by a significant concentration of *n*-butyl which arises by direct photocleavage of the tin–carbon bond. This problem was much less severe with hexamethylditin, no trace of $CH_3\cdot$ radicals being detectable in this system.
(20) After allowing for the difference in the spin and gyromagnetic ratio of deuterium, the EPR parameters for **4** and **5** were in agreement with those reported previously for 3-butenyl.[2f]
(21) Kochi, J. K.; Krusic, P. J.; Eaton, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 1877, 1879. Chen, K. S.; Edge, D. J.; Kochi, J. K. *Ibid.* **1973**, *95*, 7036.
(22) For a discussion of this point and the results of an earlier study on the interconversion of **4** and **5**, see ref 5.
(23) (a) Griller, D.; Ingold, K. U. *Int. J. Chem. Kin.* **1974**, *6*, 453. (b) Schuh, H.; Fischer, H. *Ibid.* **1976**, *8*, 341. (c) Schuh, H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2130. (d) Lehni, M.; Schuh, H.; Fischer, H. *Int. J. Chem. Kin.* **1979**, *11*, 705.
(24) Which has the same molecular weight as dideuterio-3-butenyl.
(25) Which was found to be 17% more viscous than *n*-octane.
(26) Livingston, R.; Zeldes, H.; Conradi, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 4312.
(27) N.R.C.C. Research Associate, 1978–1979.

A. Effio,[27] D. Griller, K. U. Ingold*
Division of Chemistry
National Research Council of Canada
Ottawa, Canada K1A 0R6

A. L. J. Beckwith, A. K. Serelis
Department of Organic Chemistry, University of Adelaide
Adelaide, South Australia

Received October 25, 1979

Ion Beam Studies of Organometallic Chemistry. High Energy "Sampling" of Reaction Intermediates Involved in Carbon–Carbon Bond Cleavage by Transition Metals

Sir:

Chemical transformation often involves reactive intermediates which correspond to local minima on a complex potential energy surface. Ordinarily, these species are not revealed in conventional kinetic and mechanistic studies. One approach to the characterization of such intermediates is to deprive them of sufficient energy to continue to react by deposition or formation in a low temperature matrix. An alternative method, described here, relies conversely on providing the intermediate with substantially more energy than needed for reaction. In