

relative rates is meaningful only if it is absent. An unambiguous test would require detailed isotope effect measurements as outlined by Streitwieser.<sup>24</sup> A simpler qualitative test used by us in the study of sulfoxide exchanges<sup>25</sup> requires measurement of the rates of dedeuteration in light methanol for comparison with the deuteration rates. If internal return plays a significant role, one would expect small primary isotope effects and possibly an unusual change in the relative rates of the diastereotopic protons. In fact, the backward exchange of H<sub>F</sub> showed isotope effects of the order expected for a rate-determining proton abstraction accompanied by a solvent isotope effect of ~2.<sup>26</sup> The reverse exchange of H<sub>S</sub> showed a smaller overall decrease as has been observed in several exchanges of ketones. Both Werstiuk<sup>28</sup> and Lamaty<sup>15</sup> have confirmed the original observations of Thomas et al.<sup>29</sup> that the stereoselectivity is much less in the reverse than forward (deuteration) exchange. This effect has been attributed to reversibility during exchange in the light solvent, a conclusion which appears qualitatively correct.<sup>30</sup> Thus, the relative rates of deuteration give no indication of the presence of internal return.

The only reasonable explanation for the observed 290:1 rate ratio in the exchange of **2** is the effect of stereoelectronic control. The stereoselectivity is in marked contrast to its virtually negligible magnitude in the studies involving cyclohexanones. The contrast arises not from a failure of the principle of stereoelectronic control in the latter instance, but a difference in the ability of the ketones to reveal its importance. In any organic reaction involving a stereochemical effect, its presence is usually revealed by those molecules having structural constraints which allow only certain specific conformations in the transition states. As both Valls and Tomaranoff<sup>31</sup> and House<sup>10</sup> have pointed out, the reaction of a cyclohexanone enolate can proceed by two transition states, both of which involve perpendicular attack<sup>32</sup> of the electrophile, and their energy differences result from the differences in strain in the chair and boat conformers produced therefrom. In the exchange of **2**, the enolate involved is constrained in a twist-boat conformation and its protonation from either side must lead to the single product **2**. This prescribed course of reaction will require the transition states to contain some of the sp<sup>3</sup> character of the two carbanions A and B.<sup>33</sup> In A, maximum overlap of the carbanion with the carbonyl occurs while, in B, overlap will be much decreased by the near orthogonality of the sp<sup>3</sup> and π orbitals. Thus, resonance stabilization of A will be much greater than that of B as is reflected experimentally in the stereoselectivity.

This effect has been predicted in a recent paper by Wolfe, Schlegel, Csizmadia, and Bernardi.<sup>34</sup> Using ab initio MO calculations, they calculated A to be more stable than B by 18 kcal/mol.<sup>35</sup> The qualitative agreement between experiment and theory provides an indication of the real potential of stereoelectronic control. Its influence on the rates of exchange could, in principle, result in much larger stereoselectivities, provided the ketone structure or its macroscopic environment<sup>36</sup> produces the requisite geometry in Figure 1, as well as a greater resistance to any change in geometry.

**Acknowledgments.** The authors thank the National Research Council of Canada for their financial support. We are particularly indebted to Professor Deslongchamps for the twistanone used in this work.

## References and Notes

- (1) H. Burgl, J. D. Dunlitz, and E. Shefter, *J. Am. Chem. Soc.*, **95**, 5065 (1973).
- (2) H. B. Burgl, J. M. Lehn, and G. Wipff, *J. Am. Chem. Soc.*, **96**, 1956 (1974); H. B. Burgl, J. D. Dunlitz, G. Wipff, and J. M. Lehn, *Tetrahedron*, **30**, 1563 (1974).
- (3) J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 738 (1976). For a related analysis of the ring closure of enolate anions, see J. E. Baldwin, *ibid.*, 233 (1977).

- (4) P. Deslongchamps, R. Chenevert, R. J. Taillefer, C. Moreau, and J. K. Saunders, *Can. J. Chem.*, **53**, 1601 (1975); P. Deslongchamps, S. Dube, C. Lebreux, D. R. Patterson, and R. J. Taillefer, *ibid.*, **53**, 2791 (1975); P. Deslongchamps and R. J. Taillefer, *ibid.*, **53**, 3029 (1975), and references therein.
- (5) Elie<sup>9</sup> defines the stereoelectronic factor as "the conformational requirements of the groups involved in the reaction".
- (6) E. L. Elie, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, p 139.
- (7) J. M. Lehn and G. Wipff, *J. Am. Chem. Soc.*, **96**, 4048 (1974).
- (8) E. J. Corey and R. A. Snee, *J. Am. Chem. Soc.*, **78**, 6269 (1956).
- (9) J. P. Schaefer and D. S. Weinberg, *Tetrahedron Lett.*, 1801 (1965).
- (10) H. O. House, B. A. Terfertiller, and H. D. Olmstead, *J. Org. Chem.*, **33**, 935 (1968).
- (11) G. B. Trimitsis and E. M. van Dam, *J. Chem. Soc., Chem. Commun.*, 610 (1974).
- (12) J. A. Feather and V. Gold, *J. Chem. Soc.*, 1752 (1965).
- (13) J. Fishman, *J. Org. Chem.*, **31**, 520 (1966).
- (14) F. G. Bordwell and R. G. Scamehorn, *J. Am. Chem. Soc.*, **90**, 6749 (1968).
- (15) G. Lamaty in "Isotope Effects in Organic Chemistry", Vol. 2, E. Bunce and C. C. Lee, Ed., Elsevier, Amsterdam, 1976, p 71.
- (16) R. R. Fraser and P. J. Champagne, *Can. J. Chem.*, **54**, 3809 (1976). For a similar effect in a nitrosamine, see R. R. Fraser and L. K. Ng, *J. Am. Chem. Soc.*, **98**, 5895 (1976).
- (17) The proper name for compound **2** is tricyclo[4.4.0.0<sup>3,8</sup>]decan-4-one.
- (18) Twistan-4-one (**2**) was prepared by Gauthier and Deslongchamps, *Can. J. Chem.*, **45**, 297 (1967), who provided us with a sample. Sublimation before use gave a solid whose melting point and spectral properties confirmed its structure.
- (19) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Oxford, 1969, pp 280-294.
- (20) Effects of hybridization, angle strain, and torsional interactions would influence the absolute rates, but not the relative rates, since both protons exchange via a common enol or enolate. For a clear discussion of the mechanism of the exchange reaction, see G. A. Abad, S. P. Jindall, and T. T. Tidwell, *J. Am. Chem. Soc.*, **95**, 6326 (1973).
- (21) R. R. Fraser and F. J. Schuber, *Chem. Commun.*, 1474 (1969); R. R. Fraser and F. J. Schuber, *Can. J. Chem.*, **48**, 633 (1970).
- (22) The decrease in the second-order rate constants for the exchange of each proton was approximately tenfold, a result consistent only with a general base-catalyzed mechanism of exchange, and, since a general base-catalyzed reaction requires formation of the anion in the rate-determining step, this is evidence against any significant amount of internal return.
- (23) D. H. Hunter in "Isotopes in Organic Chemistry", Vol. 1, E. Bunce and C. C. Lee, Ed., Elsevier, Amsterdam, 1975, p 135.
- (24) A. Streitwieser, Jr., P. H. Owens, G. Sonnichsen, W. K. Smith, G. R. Ziller, H. M. Niemeyer, and T. L. Kruger, *J. Am. Chem. Soc.*, **95**, 4254 (1973).
- (25) L. K. Ng, Ph.D. Thesis, University of Ottawa, 1976.
- (26) A value of 2.2 was found for  $k_2(\text{MeOD})/k_2(\text{MeOH})$  in the deuterium exchange of 9-methylfluorene.<sup>27</sup>
- (27) A. Streitwieser, Jr., W. B. Hollyhead, H. H. Pudjaatmaka, P. H. Owens, T. L. Kruger, P. A. Rubenstein, R. H. MacQuarrie, M. L. Browka, W. J. C. Chu, and H. M. Niemeyer, *J. Am. Chem. Soc.*, **93**, 5088 (1971).
- (28) S. Banerjee and N. H. Werstiuk, *Can. J. Chem.*, **53**, 1099 (1975).
- (29) A. F. Thomas, R. A. Schneider, and J. Meinwald, *J. Am. Chem. Soc.*, **89**, 68 (1967).
- (30) The analyses of Werstiuk<sup>28</sup> and Lamaty,<sup>15</sup> which employ a computer fit of the rate data using a number of assumptions including the absence of a secondary isotope effect, cannot be quantitatively assessed at this time.
- (31) J. Valls and E. Toromanoff, *Bull. Soc. Chim. Fr.*, 758 (1961).
- (32) For a broader discussion of stereoelectronic control and "perpendicular attack", see L. Velluz, J. Valls, and G. Nominee, *Angew. Chem., Int. Ed. Engl.*, **4**, 181 (1965).
- (33) The proportion of sp<sup>3</sup> character will presumably be small as in other reactions of enolates.<sup>10</sup>
- (34) S. Wolfe, H. B. Schlegel, I. G. Czizmadia, and F. Bernardi, *Can. J. Chem.*, **53**, 3365 (1975).
- (35) Such a pair of transition states, if experimentally attainable, would give rise to a rate ratio of 10<sup>13</sup>:1.
- (36) The importance of stereoelectronic control in enzyme-catalyzed reactions such as transamination is at present unknown.

R. R. Fraser,\* Philippe J. Champagne

Department of Chemistry, University of Ottawa  
Ottawa K1N 6N5, Canada

Received September 26, 1977

## Continuous Wave CO<sub>2</sub> Laser Induced Chemistry of Diborane. A Thermal Reaction

Sir:

The idea of using lasers in chemical synthesis to open reaction channels not accessible at thermal equilibrium is attractive. Bachmann, Nöth, Rinck, and Kompa<sup>1</sup> generated con-

**Table I.** Chopped and Unchopped CW-CO<sub>2</sub> Laser Irradiation of B<sub>2</sub>H<sub>6</sub> Comparison at 410-Torr B<sub>2</sub>H<sub>6</sub> Initial Pressure

Run	Chopper frequency, Hz	Laser power, W	Window loss, W	Power to sample during open time, W	Intensity to sample during open time, W/cm <sup>2</sup> <sup>a</sup>	Total run time, s <sup>b</sup>	Pentaborane yield, Torr	B <sub>10</sub> H <sub>14</sub> yield, mg <sup>c</sup>	B <sub>2</sub> H <sub>6</sub> consumed, Torr
1	Open	8.6	0.6	8	12.6	660	40	7.5	178
2	Open	8.6	0.6	8	12.6	325	38	3.8	126
3	Open	8.6	0.6	8	12.6	313	38	3.9	126
4	25	8.6	0.6	8	12.6	685	11	None	22
5	38	8.6	0.6	8	12.6	660	9	None	16
6	1600	8.6	0.6	8	12.6	685	4	None	10
7	Open	4.3	0.4	3.9	6.0	660	7	None	20
8	45	12.6	0.9	11.7	18.4	685	22	0.4	64
9	41	13.0	1.0	12.0	18.9	660	24		59
10	Open	6.6	0.5	6.1	9.6	660	28	1.2	80

<sup>a</sup> Based upon 0.9-cm beam diameter. <sup>b</sup> When chopping, the effective irradiation time is run time multiplied by open fraction. <sup>c</sup> (BH)<sub>n</sub> yields were not determined. (BH)<sub>n</sub> was not visible when there was no B<sub>10</sub>H<sub>14</sub>.

siderable attention in 1974 when they reported the use of a tuned CW-CO<sub>2</sub> laser to synthesize larger molecules, including B<sub>20</sub>H<sub>16</sub> (icosaborane), B<sub>10</sub>H<sub>14</sub> (decaborane), and B<sub>5</sub>H<sub>9</sub> (pentaborane-9) from diborane. They reported that B<sub>20</sub>H<sub>16</sub>, essentially the sole reported product in 11 out of 14 experiments, was produced in a chain process. Furthermore, B<sub>10</sub>H<sub>14</sub> and B<sub>5</sub>H<sub>9</sub> were said to have lower probability of production and occurred in the product mixture in only 3 out of 14 experiments. Since B<sub>4</sub>H<sub>10</sub> and B<sub>5</sub>H<sub>11</sub>, normally found among the products of B<sub>2</sub>H<sub>6</sub> pyrolysis experiments,<sup>2</sup> were not detected and the reaction vessel temperature did not increase, it was concluded that the reactions were initiated by a controlled vibrational excitation.

Previous studies<sup>3</sup> in our laboratory have revealed no evidence for the production of B<sub>20</sub>H<sub>16</sub> under similar conditions. A yellow white solid was produced that has characteristics similar to B<sub>20</sub>H<sub>16</sub> (except for melting point and color).<sup>4</sup> The melting point of the hygroscopic solid was determined in a drybox in total. It did not melt below 250 °C, whereas B<sub>20</sub>H<sub>16</sub> melts at 199 °C. The infrared analysis of the solid was performed upon deposits on the window after removing H<sub>2</sub>, B<sub>5</sub>H<sub>9</sub>, B<sub>5</sub>H<sub>11</sub>, B<sub>2</sub>H<sub>6</sub>, and B<sub>10</sub>H<sub>14</sub>. It was not required to open the cell for the analysis. The spectrum was found to be identical with that reported by Rinck<sup>5</sup> and is characteristic of a B-H stretch. This substance was characterized as (BH)<sub>n</sub> polymer.<sup>6</sup> It was further determined that a large number of photons were required to produce the product molecules, especially B<sub>10</sub>H<sub>14</sub> (~10<sup>2</sup>-10<sup>4</sup>). These large photon requirements suggested a complex and/or thermal mechanism.

The present work was carried out to determine if vibrationally excited molecules produced by multiple photon absorption were involved directly or if a thermal process was taking place subsequent to vibration-translational energy transfer from the laser excited B<sub>2</sub>H<sub>6</sub>. To make this distinction the laser beam was chopped with a slotted wheel (2.54-cm slots, 2.85-cm teeth, 47.1% open) driven by a variable dc motor. The procedure for preparation and analysis of samples in the cells has been described previously.<sup>3</sup> The laser was tuned to the (R(16), 00° 1-10° 0) line at 973 cm<sup>-1</sup>.

Table I compares the chopped and unchopped results at 410-Torr initial pressure. Comparing the first six listings one notes that chopping inhibits reaction substantially under our experimental conditions. However, the most important result is the fact that, when the same number of photons was passed through the system at the same power and intensity for unchopped (open) and chopped runs, the same result was not produced (runs 2 and 3 vs. runs 4 and 5). This is inconsistent with predominantly vibrationally controlled chemical processes. The results can be interpreted in terms of a thermally derived process in which the reaction rate is dependent upon the temperature within the beam envelope. Using the formu-

lation of Steverding et al.<sup>7</sup> a photoabsorption cross section for B<sub>2</sub>H<sub>6</sub> of 3 × 10<sup>-20</sup> cm<sup>2</sup> derived from its infrared spectrum, and a calculated diffusion coefficient of 1 × 10<sup>-4</sup> m<sup>2</sup>/s, we estimate the temperature in the beam envelope to be 500 K. This estimated temperature is consistent with thermally derived processes involving diborane to produce the products found. Comparisons of chopped runs 4-6 with unchopped runs 7 and 8, chopped runs 8 and 9 with unchopped run 10 indicates that average intensity (or average temperature) appears to govern the product yield.

As additional evidence we have carried out sensitized experiments involving the laser irradiation of SF<sub>6</sub> and B<sub>2</sub>H<sub>6</sub> mixtures. SF<sub>6</sub> (11 Torr) was added to B<sub>2</sub>H<sub>6</sub> (400 Torr) and the laser output was made resonant with the ν<sub>3</sub> (933 cm<sup>-1</sup>) fundamental of SF<sub>6</sub> by tuning to the (P(32), 00° 1-10° 0) line.<sup>8</sup> Power and intensity to the sample were maintained at 8 W and 12.6 W/cm<sup>2</sup>, respectively. The same products were found as occurred when B<sub>2</sub>H<sub>6</sub> was illuminated directly with the R-16 (973 cm<sup>-1</sup>) line.<sup>3</sup> However, the production of (BH)<sub>n</sub> was visibly greater than in the neat B<sub>2</sub>H<sub>6</sub> experiments. Upon opening the beam stop, (BH)<sub>n</sub> polymer could be initially generated in a (visibly) faster reaction than those leading to other products. This faster reaction ceased quickly although the beam was on. Interrupting the beam for a short time and opening the beam stop again could generate another flurry of polymer. No reaction was found when 400 Torr of neat B<sub>2</sub>H<sub>6</sub> was irradiated under these conditions. It would seem to follow that these reactions must be thermal because a V-T transfer is required for the energy to reach the B<sub>2</sub>H<sub>6</sub>.

The faster reaction producing (BH)<sub>n</sub> under sensitized conditions is interesting especially at these high pressures. The same results were found at 25 Torr of B<sub>2</sub>H<sub>6</sub> with 5 Torr of SF<sub>6</sub> using the P-20 (944.2 cm<sup>-1</sup>) line with 6.1-W power and 15.9-W/cm<sup>2</sup> intensity. The absorption cross section of SF<sub>6</sub> is several orders of magnitude greater than B<sub>2</sub>H<sub>6</sub> and results in total energy deposition within a few millimeters path length. Even though it would seem a V-T transfer is required to produce this faster reaction leading to (BH)<sub>n</sub>, the nature of this process is open to question and requires future study. High intensity pulsed CO<sub>2</sub> laser irradiations of 50-400 Torr of neat B<sub>2</sub>H<sub>6</sub> with the R-16 line have also been reported to result predominantly in formation of the yellow white polymeric solids in a faster reaction.<sup>9</sup>

**Acknowledgment.** This work was supported by the U.S. Army Research Office (Contract No. DAAG29-77-M-0099). We thank Professor R. N. Zitter of the Southern Illinois University Department of Physics and Astronomy for the suggestion of a chopping experiment, and R. Shatas of the Physical Sciences Directorate, Redstone Arsenal, Ala., for his helpful discussions.

## References and Notes

- (1) H. R. Bachmann, H. Nöth, R. Rinck, and K. L. Kompa, *Chem. Phys. Lett.*, **29**, 627 (1974).
- (2) L. H. Long, *Prog. Inorg. Chem.*, **15**, 1 (1972).
- (3) S. Shatas, D. Gregory, R. Shatas, and C. Riley, *Inorg. Chem.*, in press.
- (4) H. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **85**, 3505 (1963).
- (5) R. Rinck, "IR-Laserphotochemie von Borverbindungen", Ph.D. Dissertation, Ludwig-Maximilians-Universität, München, 1976, p 95.
- (6) I. Shapiro and R. E. Williams, *J. Am. Chem. Soc.*, **81**, 4787 (1959).
- (7) B. Steverding, H. P. Dudel, and F. P. Gibson, *J. Appl. Phys.*, **48**, 1195 (1977). For CW application, private communication.
- (8) T. Shimanouchi, "Tables of Molecular Vibrational Frequencies", Part 3, U. S. National Reference Data Series National Bureau of Standards, Vol. 17, 1968, p 11.
- (9) R. A. Shatas, J. A. Merritt, R. I. Greenberg, L. C. Robertson, G. A. Tanton, H. C. Meyer, and Clyde Riley, "Infrared Laser Controlled Borane Synthesis", 5th Conference on Chemical and Molecular Lasers, St. Louis, Mo., 1977.

C. Riley,\* S. Shatas, Valerie Arkle

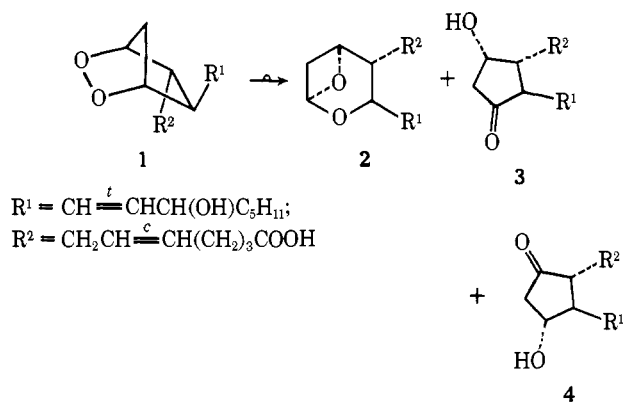
Department of Chemistry  
The University of Alabama in Huntsville  
Huntsville, Alabama 35807

Received September 6, 1977

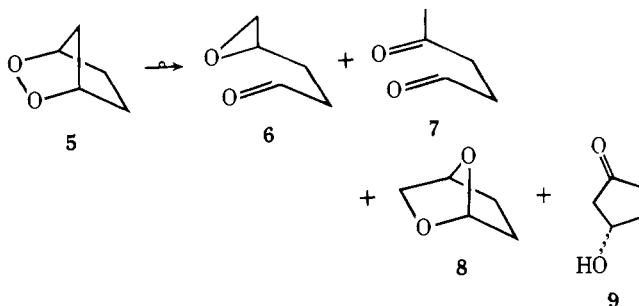
### Prostaglandin Endoperoxides. 6. A Polar Transition State in the Thermal Rearrangement of 2,3-Dioxabicyclo[2.2.1]heptane<sup>1</sup>

Sir:

Prostaglandin (PG) endoperoxides<sup>2,3</sup> (e.g., **1**) are a branch point in the oxidative transformation of polyunsaturated fatty acids into a vast array of physiologically active metabolites such as thromboxane A<sub>2</sub> (**2**),<sup>4</sup> PGD<sub>2</sub> (**3**), and PGE<sub>2</sub> (**4**).<sup>2,3</sup> We



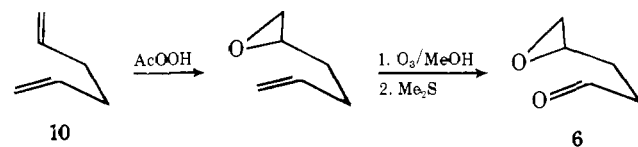
recently reported the first nonenzymatic synthesis of bona fide, fully characterized derivatives of the 2,3-dioxabicyclo[2.2.1]-heptane heterobicyclic ring system,<sup>1c</sup> and a synthesis of the parent compound **5**.<sup>1e</sup> A thorough examination of the chemistry of **5** was initiated to provide a basis for interpreting the complex biochemistry of PG endoperoxides. We now report that (a) the model endoperoxide **5** rearranges thermally to afford **6-9**; (b) the relative yields of these products are strongly



solvent dependent; and (c) the rate of decomposition increases with solvent polarity and is exceptionally rapid in protic solvents. Solvent effects on the thermal reactions of **5** result primarily from an extraordinary dependence of the rate of rearrangement to levinaldehyde (**7**) on solvent polarity.

Extraordinary reactivity was postulated for PG endoperoxides owing to the strained bicyclic structure of their peroxide nucleus **5**. Instability at room temperature was predicted.<sup>5</sup> More recently, PG endoperoxides, prepared enzymatically, were isolated.<sup>3</sup> As expected, these endoperoxides are thermally labile. In nonpolar organic solution (1:1 light petroleum-ether), 9 $\alpha$ ,11 $\alpha$ -epidioxo-15(*S*)-hydroxy-13-*trans*-prostenoic acid decomposes with a half-life of 2.7 h at 20 °C. In aqueous medium, at pH 4-8, the half-life is only 30 min at 20 °C.<sup>3b</sup> PG-endoperoxide-like derivatives of **5** were also obtained nonenzymatically, by autoxidation of methyl linolenate, and were observed to decompose thermally with a half-life of 3.3 h at 80 °C.<sup>6</sup>

Thermal decomposition of **5** was monitored by <sup>1</sup>H NMR and GLC.<sup>7</sup> Products **7**, **8**, and **9** were identified by spectral and GLC comparison with authentic samples, prepared by reported procedures.<sup>8</sup> The identity of the epoxy aldehyde (**6**), a new

Table I. Thermal Decomposition of **5**<sup>a</sup>

Entry	Reaction solvent	<i>D</i> <sup>b</sup>	Reaction temp °C	<i>t</i> <sub>1/2</sub> , <sup>c</sup> h	Products, mol % <sup>d</sup>			
					6	7	8	9
A	Cyclohexane	1.94	73	5.7	97	2	1	0
B	CCl <sub>4</sub>	2.13	73	4.1	87	10	3	0
C	Benzene- <i>d</i> <sub>6</sub>	2.18	73	2.9	86	11	3	0
D	Chlorobenzene	4.85	73	2.4	85	15	0	0
X	CD <sub>3</sub> COOD	6.63	73	0.22	0	100	0	0
E	CICD <sub>2</sub> CD <sub>2</sub> Cl	7.94	73	2.1	54	42	4	0
F	2-Butanone	14.35	73	1.5	63	35	2	0
G	CD <sub>3</sub> CN	28	73	1.3	40	59	1	0
Y	D <sub>2</sub> O	74	40	0.12	0	72	0	28

<sup>a</sup> The concentration of **5** was ~0.5 M for each experiment. For entry F one run was conducted under air, another under oxygen, and a third deoxygenated by three freeze-pump-thaw cycles. The same rate of decomposition of **5** was observed for each run. Therefore, all other experiments were conducted under air. For entries A, X, and Y, solvents were freed of most catalytic impurities, especially metal ions, by stirring with Na<sub>2</sub>EDTA for 1 week followed by a low temperature molecular distillation. Furthermore, all glassware, including <sup>1</sup>H NMR tubes and the receivers into which **5** was sublimed prior to use, were scrupulously cleaned with Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-H<sub>2</sub>SO<sub>4</sub> followed by NH<sub>4</sub>OH (1 day) and Na<sub>2</sub>EDTA (1 day), rinsed with distilled water, and dried. Omission of the Na<sub>2</sub>EDTA for solvent purification and washing of glassware did not change the rate observed for decomposition of **5**. <sup>b</sup> Corrected for temperature. <sup>c</sup> Half-life calculated from the corresponding first-order rate constants (see Table II). <sup>d</sup> Near-quantitative overall yields determined by GLC analysis with *n*-undecane or diglyme as internal standard.