systematically from a tetrahedral reactant-like transition state for $n_1 \sim 1$ to trigonal bipyramidal for symmetric models ($n_1 \sim 0.5$) to a tetrahedral product-like model for $n_1 \sim 0$. All other variables were taken equal to reactant (or product) values selected from standard sources.[14] A zero or imaginary reaction coordinate frequency $\nu_L^{\ddagger}$ was obtained by introducing an interaction constant F_{12} equal to or greater than $(F_1F_2)^{1/2}$, respectively.[15]

The calculated carbon-14 and chlorine-37 isotope effects for reaction 1 are shown in Figure 1 for Y equals O (I), Cl (II), and S (III). As can clearly be seen, the carbon isotope effect goes through a maximum as n_1 decreases. The results support the qualitative suggestion[8] that an S$_N$2 reaction can be viewed as an "RCH_2 group" transfer from X to Y, with mechanistic implications similar to those of hydrogen-transfer reactions.

Compared to the symmetric chlorine exchange reaction, where the maximum isotope effect occurs for $n_1 = 0.5$ (Figure 1, curve II), one can see that the transition state corresponding to the maximum isotope effect becomes more reactant-like, $n_1 > 0.5$ (curve I) as the forming bond (C–O) becomes stronger than the rupturing C–Cl bond, or more product-like, $n_1 < 0.5$ (curve III), as the forming bond (C–S) becomes weaker than the rupturing C–Cl bond. This trend is consistent with the Hammond postulate.[16]

The chlorine isotope effect, on the other hand, increases continuously as one goes from a reactant-like to a product-like transition state (*i.e.*, as n_1 decreases). The chlorine isotope effect for a forming O–C bond (curve I) is calculated to be somewhat larger than for a forming S–C bond (curve III), in contrast to the recent experimental results of Grimsrud and Taylor.[17] However, the calculated isotope effects for these two cases are not significantly different, and solvation of the leaving group and/or nucleophile may appreciably affect the chlorine isotope effect but would not be expected to alter the trends in the carbon isotope effect.

The experimental[9] isotope effects for solvolysis (curve I, Y = O) are: $k/k^* \sim 1.08$ for carbon-14 and 1.008 for chlorine-37. The results in Table II show that a more realistic reaction coordinate frequency ($\nu_L^{\ddagger}$ imaginary rather than zero) yields calculated carbon-14 and chlorine-37 isotope effects in better agreement with experiment. Details of the calculations, including cutoff procedures and comparisons with available experimental data, will be published subsequently.

Table II. Effect of Reaction Coordinate Frequency on Calculated Kinetic Isotope Effects at 30° for Reaction 1 of Text[a]

$\nu_L^{\ddagger}$	k^{12}/k^{14}	k^{35}/k^{37}
0	1.05911	1.01289
139*i*	1.07310	1.01087
204*i*	1.08159	1.00926
264*i*	1.08686	1.00825

[a] Cutoff model **2** (see Table I) was used with $n_1 = 0.6$ and $n_2 = 0.4$.

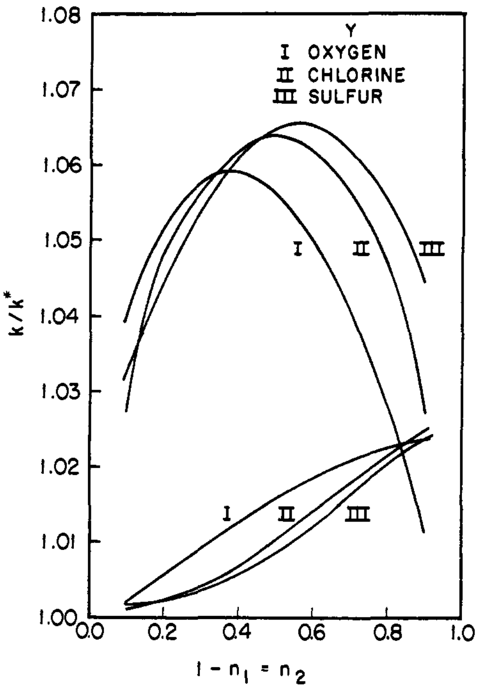

Figure 1. Calculated carbon-14 (upper curves) and chlorine-37 (lower curves) isotope effects as a function of bond order for reaction 1 using cutoff model 1.

To our knowledge, no heavy-atom kinetic isotope effect results have been reported which illustrate the bell-shaped behavior shown in Figure 1. Experiments are being carried out in this laboratory to test this concept.

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[14] G. Herzberg, "Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945; G. W. Wheland, "Advanced Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1960; E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955.

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[17] E. P. Grimsrud and J. W. Taylor, *ibid.*, **92**, 739 (1970).

[18] (a) NDEA Fellow, 1965–1968; Phillips Petroleum Fellow, 1968–1969; (b) NDEA Fellow, 1969–1971; NSF Trainee, 1971–1972; (c) NSF Trainee, 1971–1972.

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Synthesis and Chemistry of α-Lactones[1]

Sir:

Synthesis of α-lactones poses a long-standing challenge. α-Lactones have been invoked as intermediates in such diverse transformations as nucleophilic displacements,[2] free-radical processes,[3] thermal eliminations,[4] and photochemical reactions.[5] A variety of in-

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[1] Photochemical Transformations. XLIV. Cyclic Peroxides. VII.

[2] W. A. Cowdrey, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1208 (1937); S. Winstein and H. J. Lucas, *J. Amer. Chem. Soc.*, **61**, 1576 (1939); E. Grunwald and S. Winstein, *ibid.*, **70**, 841 (1948); F. G. Bordwell and A. C. Knipe, *J. Org. Chem.*, **35**, 2956 (1970).

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[4] D. G. H. Ballard and B. J. Tighe, *J. Chem. Soc. B*, 702 (1967); B. J. Tighe, *Chem. Ind.* (*London*), 1837 (1969).

[5] W. Adam and R. Rucktäschel, *J. Amer. Chem. Soc.*, **93**, 557 (1971).

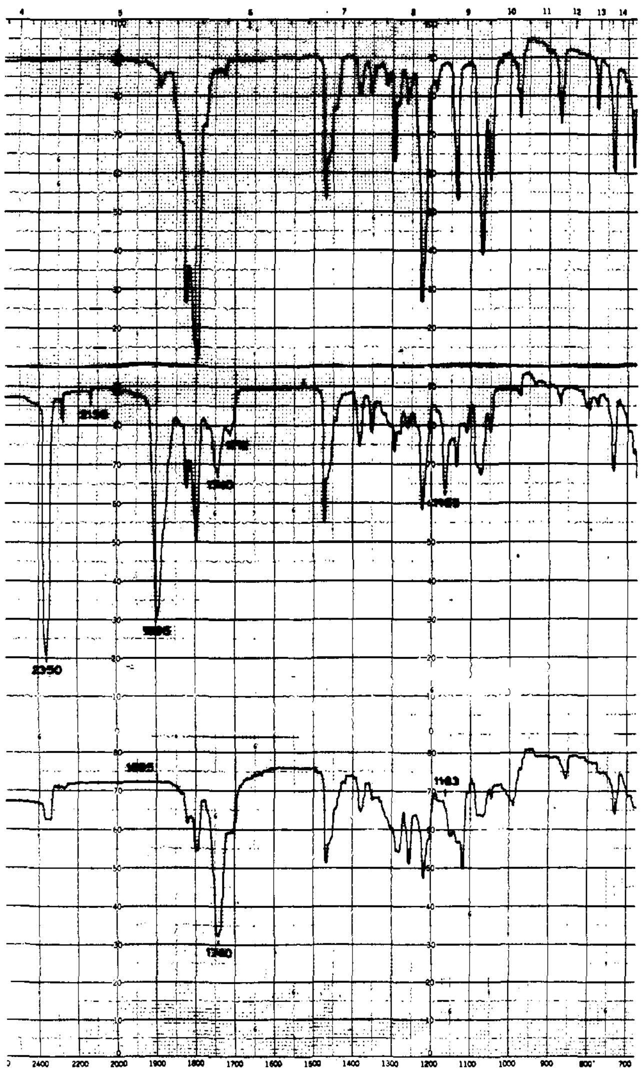
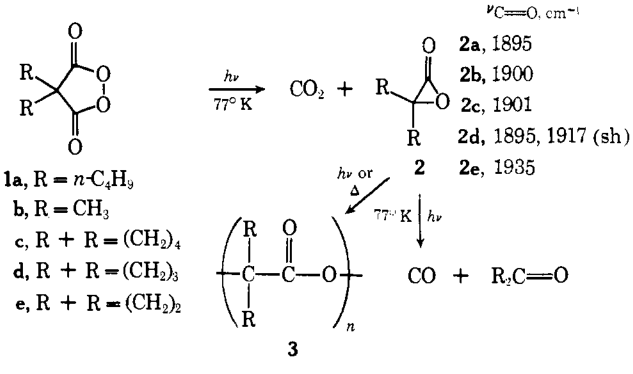


Figure 1. Infrared spectrum of neat **1a** at 77°K before irradiation (top), after irradiation for 15 min (center), and after warming to −50° and recooling to 77°K.

genious approaches have been used in attempts to generate α-lactones,[6] but characterization of these elusive compounds has been limited to a single nmr observation and the preparation of several derivatives *in situ*.[6] We wish to report a facile, high-yield photochemical synthesis of α-lactones under conditions which permit spectroscopic observation and investigation of the chemistry and photochemistry of these intriguing molecules.



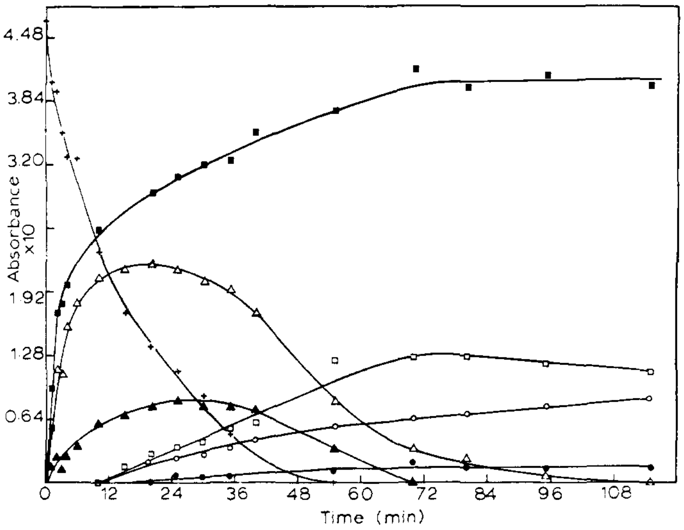


Figure 2. Plot of absorbance of significant absorption bands as a function of irradiation time for **1a** at 77°K: +, $\nu_{C=O}$ **1a**; ■, CO_2 (2350 cm⁻¹); △, $\nu_{C=O}$ **2a** (1895) cm⁻¹); ▲, ν_{C-O} **2a** (1163 cm⁻¹); □, $\nu_{C=O}$ polyester **3a**; ○, $\nu_{C=O}$ 5-nonanone; ●, CO (2138 cm⁻¹).

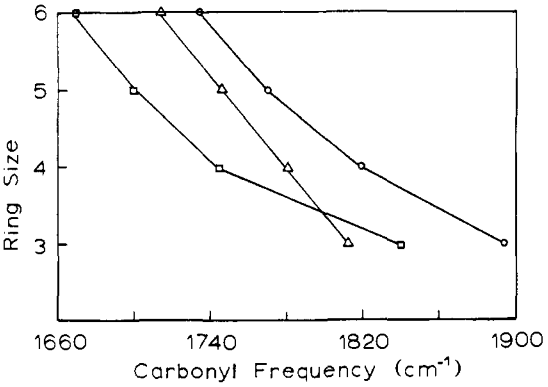


Figure 3. Plot of carbonyl stretching frequency (cm⁻¹) as a function of ring size for lactams (□), ketones (△), and lactones (○).

Irradiation of 4,4-di-*n*-butyl-1,2-dioxolane-3,5-dione (**1a**)[5] as the neat liquid at 77°K in an infrared cell[7] equipped with a vacuum shroud and dewar using an 800-W high-pressure mercury arc with quartz optics led to rapid disappearance of the starting material and concurrent appearance of carbon dioxide and the α-lactone **2a**. The α-lactone **2a** shows carbonyl absorption at 1895 cm⁻¹ and C–O absorption at 1163 cm⁻¹ (Figure 1). Plots of the intensity of the new infrared absorption bands (Figure 2) show that the α-lactone and carbon dioxide are the only primary photoproducts. Bands at 2138, 1740, and 1712 cm⁻¹ are associated with secondary photoproducts derived from the α-lactone. The bands at 2138 and 1712 cm⁻¹ appear at the same rate (Figure 2). The band at 2138 cm⁻¹ is due to carbon monoxide; the 1712-cm⁻¹ absorption is attributed to 5-nonanone.[8] Decarbonylation is thus a

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(6) See, for example, R. Wheland P. D. Bartlett, *ibid.*, **92**, 6057 (1970).

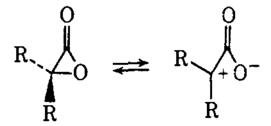
(7) This is the same apparatus used in previous studies: O. L. Chapman and J. D. Lassila, *ibid.*, **90**, 2449 (1968); P. J. Nelson, D. Ostrem, J. D. Lassila, and O. L. Chapman, *J. Org. Chem.*, **34**, 811 (1969); and subsequent papers in this series.

(8) The position of the carbonyl is that of the authentic material under the same conditions. Additional evidence that the other product of the decarbonylation is the ketone comes from the observation that decarbonylation of **2d** gives a product with $\nu_{C=O}$ 1775 cm⁻¹ (cyclobutanone). At room temperature, 5-nonanone is a product of the irradiation of **1a**. It is probable that in this case the ketone has a differ-

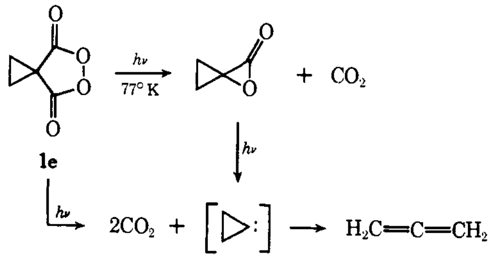
primary photochemical reaction of the α-lactone. A second photochemical reaction of the α-lactone leads to the product with the 1740-cm^{-1} absorption. The infrared spectrum of this product identifies it as the polyester **3a** which is the major product from the room temperature irradiation of **1a**.[5] Polyester **3a** is also formed when the α-lactone is warmed above −100°. This result is in accord with mechanisms previously suggested for polyester formation.[5]

Irradiation of peroxides **1b–e** at 77°K gives in each case an α-lactone and carbon dioxide. Warming above −100° again converts the α-lactones to polyesters. Irradiation of α-lactones (**2b–d**) gives carbon monoxide (2138 cm^{-1}) and the corresponding ketones.

The carbonyl stretching frequency of the α-lactones clearly shows that at 77°K they exist as the closed α-lactone structure rather than as the zwitterion. The position of $\nu_{C=O}$ is quite reasonable (Figure 3). The thermal instability of the α-lactones above −100° suggests that there is a small activation barrier between the α-lactone and the zwitterion. The very low temperatures at which the α-lactones polymerize also accounts very directly for the failures encountered in earlier attempts to observe α-lactones at temperatures as low as Dry Ice–acetone mixtures.[6] The thermal polymerization of α-lactones is in accord with earlier postulates.[3,5] The photochemical decarbonylation and polymerization of the α-lactone are unexceptional. Photodecarbonylation has been observed in α-lactams.[9]



The spirocyclopropyl α-lactone is especially interesting. The carbonyl frequency (1935 cm^{-1}) indicates a stronger than normal α-lactone carbonyl bond even though the carbonyl group bisects the cyclopropane ring in perfect fashion for conjugative overlap. Allene is a significant product in the irradiation of peroxide **1e** as well as the α-lactone. It is likely that allene is formed by way of the carbene **4**. The carbene could be formed by loss of two molecules of carbon dioxide from **1e** or by loss of carbon dioxide from the α-lactone. Preliminary evidence suggests that at 77°K the major path is that *via* the α-lactone.



Acknowledgment. The research at ISU was supported by the National Science Foundation (GP-28152X), the National Institute of Arthritis and Metabolic Diseases (AM 14624), and the Petroleum Research Fund of the American Chemical Society (5252-AC4). The research at UPR was supported by the National Science Foundation (GP-17755), the Petroleum Research Fund of the American Chemical Society (4105-A), and the A. P. Sloan Foundation.

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ent origin. At 77°K the polyester undergoes a slow conversion to carbon monoxide and ketone. It may be that polyester is the source of the small amount of ketone observed at room temperature.

(9) E. R. Talaty, A. E. Du Puy, Jr., and T. H. Golson, *Chem. Commun.*, 49 (1969).

Internal Exchange in New Group III Metalloborane Derivatives, $(CH_3)_2AlB_3H_8$ and $(CH_3)_2GaB_3H_8$

Sir:

We wish to report the syntheses and preliminary structural studies of dimethylaluminum triborane(8) and dimethylgallium triborane(8).[1] Previously the chemistry of the $B_3H_8^-$ anion[2] has been restricted to its use in the synthesis of higher boranes[3,4] and transition metal complexes.[5,6] The relatively recent development of convenient synthetic procedures[3,7] makes this reagent potentially useful for a wide variety of chemical investigations, including the synthesis of covalent main group derivatives.

The preparation of $(CH_3)_2AlB_3H_8$ and $(CH_3)_2GaB_3H_8$ involves the reaction of $(CH_3)_2GaCl$ or $(CH_3)_2AlCl$ with salts of $B_3H_8^-$. In a typical reaction, excess NaB_3H_8[2] was stirred in a vacuum with 4.7 mmol of solid $(CH_3)_2GaCl$ for 15 min at room temperature, during which time a mobile liquid was formed. The product, $(CH_3)_2GaB_3H_8$, was then purified by high-vacuum fractional distillation; it distils slowly through a −45° trap and is essentially completely condensed by a −63° trap. The yield of purified $(CH_3)_2GaB_3H_8$ was 2.95 mmol, 63%. The use of $(CH_3)_4N^+$ and $(n\text{-}C_4H_9)_4N^+$ salts of $B_3H_8^-$ produces similar yields of the product. The $(CH_3)_2AlB_3H_8$ was prepared using the same procedures and similar yields were obtained. The volatilities of these compounds suggest that they are monomers, at least in the vapor phase. As their apparent thermal stability is marginal, vapor pressure measurements are not reliable purity criteria.

$(CH_3)_2AlB_3H_8$: 0°, 13 Torr; 19°, 35 Torr

$(CH_3)_2GaB_3H_8$: 0°, 4 Torr; 24°, 13 Torr

The gas-phase infrared spectra of $(CH_3)_2AlB_3H_8$ and $(CH_3)_2GaB_3H_8$ are virtually identical in the stretching region, indicating that their vapor-phase structures are probably very similar: $(CH_3)_2AlB_3H_8$ (cm^{-1} ±10)

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(1) In accordance with IUPAC "Nomenclature of Inorganic Boron Compounds," No. 8, 1970, it appears that these compounds could be referred to by the names 2,2-dimethyl-2-aluminatetraborane(10) and 2,2-dimethyl-2-gallatetraborane(10). However, it was felt this nomenclature might be misleading.

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(6) F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *ibid.*, **7**, 2272 (1968).

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