(7) T. E. Bellas, R. G. Brownlee, and R. M. Silverstein, *Tetrahedron*, **25**, 5149 (1969).
(8) H. H. Wasserman and E. H. Barber, *J. Am. Chem. Soc.*, **91**, 3674 (1969). See also J. O. Rodin, C. A. Reece, R. M. Silverstein, V. H. Brown, and J. I. DeGraw, *J. Chem. Eng. Data*, **16**, 380 (1971).
(9) K. Mori, *Tetrahedron*, **30**, 4223 (1974).
(10) B. P. Mundy, K. B. Lipkowitz, and G. W. Dirks, *Synth. Commun.*, **5**, 7 (1975), and references cited therein.
(11) The 2-ethyl-3-methylcyclohex-2-en-1-one was prepared by hydrolysis and decarboxylation of commercial (Aldrich) 2-ethyl-3-methyl-4-carboethoxycyclohex-2-en-1-one as described: L. I. Smith and G. F. Rouault, *J. Am. Chem. Soc.*, **65**, 631 (1943). The decarboxylation reaction did not occur spontaneously under the reaction conditions reported. However, acidification of the crude reaction mixture resulted in vigorous evolution of CO_2 to afford the desired cyclohexenone **1** in 84% yield after one recycling of recovered starting material.
(12) R. K. Müller, D. Felix, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, **53**, 1479 (1970), and references cited therein.
(13) No attempt has been made to optimize the yields.
(14) To our knowledge, this reaction represents the first application of the relatively inexpensive and safe $BH_3{\cdot}Me_2S$ reagent for the reductive hydroboration of an acetylene. The use of $BH_3{\cdot}THF$ or disiamylborane in THF offered no advantage in yield or stereoselectivity and was considerably more expensive.
(15) We were unable to effect a separation of the cis and trans olefins **5** and **9** by VPC. However, an assay of the stereoselectivity of the reduction reactions was possible by an analysis of the corresponding epoxides **6** and **10** which were readily separable (see ref 7). Both **6** and **10** were contaminated with <1% of the corresponding isomer.
(16) J. G. Buchanan and H. Z. Sable in "Selective Organic Transformations", Vol. 2, B. S. Thyagarayan, Ed., Wiley, New York, N.Y., 1972, pp 8–11.
(17) Although the acetic acid was dried by reaction with acetic anhydride in the presence of a trace of *p*-TsOH and every effort maintained to exclude moisture from the reaction mixture during protonolysis of the vinylborane, the product obtained invariably contained anywhere from a trace to ~15% of *cis*-non-6-en-2-one. Reketalization afforded the desired ketal **5**.
(18) R. M. Silverstein, *J. Chem. Educ.*, **45**, 794 (1968).

Communications

Synthetic Photochemistry with the Imide System. Norrish Type II Cyclization of Alicyclic Imides[1,2]

Summary: On irradiation a series of *N*-alkyl-substituted succinimides and glutarimides readily underwent photocyclization to afford ketolactams with ring enlargement by the two-carbon unit derived from the side chain in moderate yields; the efficiencies of the photoreactions of the alicyclic imides were distinctly larger than that for the aromatic counterparts (phthalimides), being comparable with that for simple ketones; the Norrish type II processes were proposed as the mechanism and general synthetic utility of the reaction was discussed.

Sir: In contrast to the extensive studies on photochemistry of common carboxylic acid derivatives such as esters and amides, the photochemical behavior of imides has been scarcely investigated. As part of broadly based studies of synthetic photoreactions of carbonyl derivatives, we have recently explored reactions of the excited states of an *aromatic* imide system, phthalimides.[3] We now wish to report a scheme which characterizes the photochemistry of *alicyclic* imides, and to present evidence which indicates its general synthetic utility.

A series of N-substituted succinimides **1a–i** and glutarimides **1j–m** were irrddiated[4] and the results are listed in Table I. Each major photoproduct was purified in most runs by vacuum distillation and identified by its ir, uv, NMR, and mass spectra and elemental analysis. In all cases ketolactams having two additional carbons in their rings were readily obtained in moderate isolated yields, accompanied by some elimination products (succinimide or glutarimide, 10–30%). In a representative example, the structural assignment for **2c** was based on (i) the presence of a carbonyl [uv 283 nm (ϵ 27); ir 1700 cm^{-1}] and an amide (ir 1660 mm^{-1}); (ii) the presence of the β [NMR 3.80 ppm ($C_\beta H$, m)] and the γ [NMR ~2.6 ppm (C_γ H_2)] carbons, methyl [1.35 ppm (d)], and NH (7.05 ppm); (iii) the molecular weight and composition, $C_7H_{11}NO_2$ (mass *m/e* 141; elemental analysis). Only one isomer (cis), **2g** and **2m**, was isolated from **1g** and **1m**, respeciively, hhereas a mixture of two stereoisomers, **2h** and **2i**, were obtained from **1h** and **1i**.

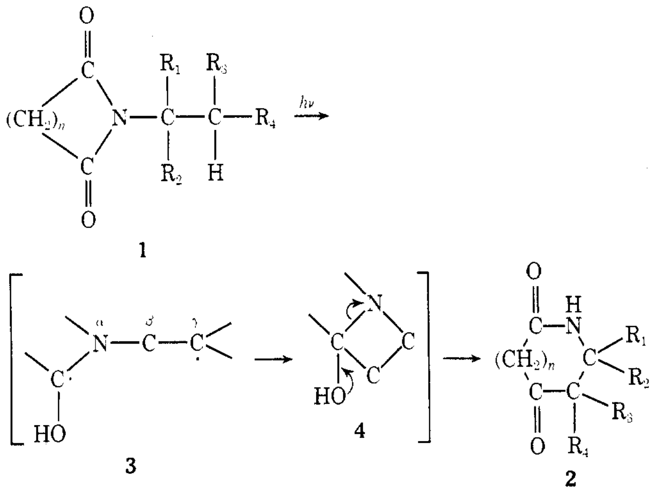
Table I
Products of Photolysis of the Cyclic Imides **1**[a]

	1				2	
Compds	R_1	R_2	R_3	R_4	%	Mp, °C
			n = 2			
a	H	H	H	H	45	139–140
b	H	H	CH_3	H	42	120–121
c	H	CH_3	H	H	56	139.5–140.5
d	H	H	C_2H_5	H	31	85–87
e	H	H	CH_3	CH_3	33	109–110
f	CH_3	CH_3	H	H	49	175–176
g	H	$-(CH_2)_3-$		H	50	192.5–193.5
h	H	$-(CH_2)_4-$		H	42	Mixture
i	H	$-(CH_2)_5-$		H	38	Mixture
			n = 3			
j	H	H	H	H	37	117–118
k	H	H	CH_3	H	52	141–142
l	H	H	C_2H_5	H	33	149–150
m	H	$-(CH_2)_3-$		H	28	220–221.5

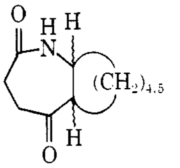
[a] A 60-W low pressure mercury lamp was used for 30 min, 10m*M* solution in acetonitrile.

The principal feature of the Norrish type II processes of the alicyclic imides is not the elimination but rather the cyclization forming ketolactams with ring enlargement by the two-carbon unit derived from the side chain (Scheme I). Quantum yield of the formation of **2a** was 0.64,[7] which is notably larger than that for the reactions of phthalimides, the aromatic counterparts, by a factor of 50,[8] indicating practical efficiency of the photolysis of the alicyclic imide system. General synthetic potential of the reaction on the basis of structural variation of the substrates is as follows.

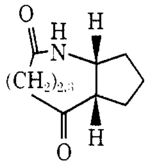
Scheme I



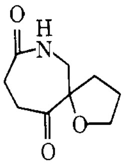
Variation of the N substituents (including heteroatoms and cyclic systems) may lead to a wide variety of products. For example, *N*-tetrayydrofurfurylsuccinimide gave the expected spiro azepinone **5** (mp 96–98°, 27%). In view of their multifunctionality, these photoproducts will further be used as synthetic intermediates. By activation due to introduction of heteroatoms into the side chain, extensive type II processes seem possible involving δ (or other) hydrogen abstraction.[9] The ring size of the imides (n) could be increased beyond three. In addition, the ring may carry substituents as desired. For example, 1-ethyl-4,4-dimethylglutarimide readily produced **6** (mp 173–174°, 27%).



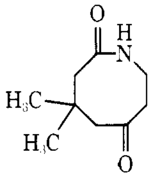
2h.i



2g.m



5



6

Piperylene quenches the formation of **2a** from **1a** indicative of a triplet intermediate. A Stern–Volmer plot in acetonitrile (up to 1 mM) is linear with a slope $k_q\tau$ = 670 M^{-1}.[12] As a plausible mechanism the biradical intermediate **3** is postulated (Scheme I) which is generally accepted in the type II processes of ketones as summarized by Wagner.[13] Such a biradical would either lead to elimination or undergo cyclization to form **4** followed by retrotransannular ring opening[14] giving rise to the ring-enlarged products **2**. Since these cyclic imides are starting materials which can be relatively easily prepared, this method may provide a novel versatile synthetic entry to otherwise rather unaccessible type of compounds including medium-sized and other various heterocyclic systems. Further synthetic scope and the mechanism of the photochemistry of the imide system are under investigation.

References and Notes

(1) Photochemistry of the Imide System. I.

(2) Photoinduced Reactions. XXIV Part XXIII: Y. Kanaoka, K. Sakai, R. Murata, and Y. Hatanaka, *Heterocycles*, **3**, 719 (1975).

(3) Y. Kanaoka and Y. Migita, *Tetrahedron Lett.*, 3693 (1974), and earlier papers cited therein.

(4) To our knowledge very few photochemical studies of aliphatic imides previously reported include vapor-phase photolysis of succinimide,[5] which is, however, of little interest from the synteetic point of view. Examination as well as the literature survey[5,6] of the uv spectra of aliphatic imides revealed that 2537-Å light of a low pressure mercury lamp is convenient for exciting the aliphatic imide carbonyl. Tests on the wavelength dependency of the formation of **2** indeed showed that only the range 230–270 nm is effective with the maximum around 240 nm in accord with the uv of **1a**.

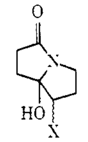
(5) G. Choudhary, A. M. Cameron, and R. A. Back, *J. Phys. Chem.*, **72**, 2289 (1968).

(6) O. H. Wheeler and O. Rosando in "The Chemistry of Amides," J. Zabicky, Ed., Interscience-Wiley, New York, N.Y., 1970, p 358.

(7) Formation of **2a** (degassed acetonitrile solution, 10 m*M*) was monitored by gas chromatography, and the quantum yield was determined by potassium ferrioxalate actinometry using 2537-Å light on a merry-go-round.

(8) Quantum yield of photocyclization of N-(*o*-tolyl)phthalimide is on the order of 0.01: Y. Kanaoka, K. Koyama and Y. Hatanaka, unpublished data.

(9) For example, photolysis of succinimides with ether and sulfide moieties in the alkyl chains gave i,[10] which are the products from δ-hydrogen ab-



i, X = OCH_3, SCH_3

straction. Maruyama and Kubo have independently reported some related results.[11]

(10) Y. Kanaoka, Y. Hatanaka, H. Nakai, Y. Sato, and T. Mizoguchi, in preparation.

(11) K. Maruyama and Y. Kubo, 33rd Annual Meeting of the Chemical Society of Japan, Tokyo, April 1975, Abstracts of Papers, III, p 1176.

(12) The quenching study was performed in degassed acetonitrile solution (10 m*M*) with 2537-Å light on a merry-go-round. From this, approximate order of τ was estimated to be 10^{-7}–10^{-8} sec.

(13) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).

(14) This cyclization–ring opening has been proposed in the phthalimide system; cf. Y. Kanaoka, Y. Migita, K. Koyama, Y. Sato, H. Nakai, and T. Mizoguchi, *Tetrahedron Lett.*, 1193 (1973).

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Received November 5, 1975

Organocopper Chemistry. The Coupling of (*E*)-2-Iodo-1-alkenyl Sulfones with Monocopper(I) Reagents

Summary: Monocopper(I) reagents (**2**) couple stereospecifically with (*E*)-2-iodo-1-alkenyl sulfones (**1**) to form β-alkylated 2-alkyl-1-alkenyl sulfones (**3**) with retained configuration.

Sir: The preparation and some of the reactions of 2-iodo- and 2-bromo-1-alkenyl sulfones has been the subject of several recent investigations.[1,2] The stereospecific organocopper coupling of vinyl iodides with organocopper reagents[3,4] has recently been reported as a method for the synthesis of alkenes of known configuration. This work prompts us to report on our preliminary results concerning the stereospecific coupling of a variety of (*E*)-2-iodo-1-alkenyl sulfones with a variety of monocopper(I) reagents.

Monoalkyl and monoarylcopper(I) reagents couple in good to excellent yields (Table I) with (*E*)-2-iodo-1-alkenyl sulfones and with complete retention of configuration. The presence of a single isomer is verified by a single set of proton absorptions in the ^1H NMR and the absence of absorptions for the isomeric structures. The assignment of configuration is based upon ^1H NMR chemical shift data and alternate synthesis.[5]