Photolysis² of a 5% (w/v) solution of I³ in methanol for 18 hr with light of wavelength >2800 Å gave⁴ a 22.5% yield of 4,4,5,5-tetramethyl-1-thiaspiro[2.2]pentane (II) [ir(CCl₄) 1445 (s), 1350 (s), 1210 cm⁻¹ (s); nmr (CDCl₃) δ 2.59 (s, 2 H), 1.14 (s, 6 H), 1.08 ppm (s, 6 H); mass spectrum (70 eV) m/e(parent ion)142], a 27.6% yield of the trans cyclic acetal III [ir (CCl₄) 1190 (s), 1065 cm⁻¹ (s); nmr (CDCl₃) δ 4.59 (s, 1 H), 3.31 (s, 3 H), 1.32 (s, 6 H), 1.16, 0.73 (s, 3 H) each), 2.41 (d, 1 H, J = 1.8 Hz), 2.47 ppm (d, 1 H, J = 1.8 Hz);mass spectrum (70 eV) m/e(parent ion) 202] and an 8.9 %yield of the *cis* cyclic acetal IV [ir (CCl₄) 1198 (s), 1065 cm^{-1} (s); nmr (CDCl₃) 4.58 (s, 1 H), 3.35 (s, 3 H), 1.26 (s, 6 H), 1.11, 0.83 (s, 3 H each), 2.23 (d, 1 H, J = 1.8Hz), 2.36 ppm (d, 1 H, J = 1.8 Hz); mass spectrum (70 eV) m/e(parent ion) 202].

Photolysis with 2537-Å light⁵ in methanol gave a 56.1% yield of the methylenecyclobutanone V as the major voltatile product,⁶ plus 7.3, 8.9, and 2.8% yields of II, III, and IV, respectively; in addition, a nonvolatile residue was formed.

Products formed by photolysis with >2800-Å light are consistent with the formation of an alkylacyl biradical resulting from a Norrish type I cleavage of the n, π^* state of the carbonyl group. The intermediate biradical can eliminate carbon monoxide to form II or undergo ring closure on the oxygen atom to form the intermediate oxacarbene VI. The formation of oxacarbenes as



intermediates in the photolysis of substituted cyclobutanones has been demonstrated.8-11

Unlike the electronic spectra of other keto sulfides, 12-15 the electronic spectrum of I gave no evidence for chargetransfer states resulting from transannular interaction of a lone pair of electrons on sulfur with the carbonyl group. Such interactions would give rise to structures such as VII and result in both perturbation of the $n-\pi^*$ carbonyl frequency and the appearance of an intense absorption band in the 240- to 270-nm region. Since the geometry of the molecule is such that significant

(2) Photolyses were performed in Pyrex vials (degassed and sealed prior to photolysis) with a Hanovia 550-W medium-pressure mercury arc.

(3) λ_{max}^{hexane} 300 (log ϵ 1.27), 314 (1.28), 265 nm (1.80).

(4) Yields reported are not those of products isolated; the mixture was analyzed by gas chromatography on a 6-ft column of 20% silicone rubber UC W98 on Diatoport S; the column was operated isothermally at 100°; analytical samples were collected at 85°

(5) An air-cooled Rayonet Photochemical reactor (Southern New England Ultraviolet Co., Middletown, Conn.) and Vycor reaction vessels were used. The light source consisted of 16 2537-Å fluorescent lamps

(6) The melting point (42–43°), ir (CCl₄) [1800 (s), 1675 cm⁻¹ (s)], and nmr (CCl₄) [δ 5.03 (s, 2 H), 1.22 (s, 12 H)] agreed with the values reported by Hamon.7

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orbital overlap will not occur, this observation is not surprising. The high-energy 265-nm band, interpreted as an n,σ^* state associated with sulfur, has been observed in the electronic spectrum of other substituted episulfides.^{16,17} Loss of sulfur was the major process which occurred upon excitation with 2537-Å light. The products resulting from the n, π^* state of the carbonyl are assumed to be a result of stray 3100-Å light associated with the 2537-Å fluorescent lamps used. The fact that loss of sulfur is the major process indicates that intermolecular and intramolecular energy transfers from the n,σ^* state to the n,π^* state of the carbonyl group are inefficient and that scission of the carbonsulfur bond is a rapid process.

The absence of V in the products from the long-wavelength photolysis showed that no interaction occurred between the carbonyl group and sulfur. The photochemistry of γ -keto sulfides has been found to be strongly influenced by the presence of a perturbed carbonyl group.¹⁵

A recent example of a photochemical reaction in which wavelength is a controlling factor is the photolysis of 3-benzoyl-2-phenyl-1-azirine.¹⁸ With light of wavelength >3340 Å, 3,5-diphenylisoxazole was formed as the major product, whereas with light of wavelength <3130 Å, 2,5-diphenyloxazole was formed. Sensitization experiments suggested that the isoxazole is formed via the (n, π^*) state of the carbonyl chromophore and that the oxazole is formed via the (n, π^*) state of the ketimine chromophore. Although the multiplicities of the excited states arising from the two chromophores in I have not been determined, a $^{3}(n,\pi^{*})$ state of the carbonyl group and a (n,σ^*) state of the sulfur atom probably account for the observed results.

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α -Lactams. VII.¹ An Insertion-Type Alkylation on α -Lactams by Action of Alkylmagnesium Halides

Sir:

Reactions of α -lactams have been reported recently¹⁻⁵ which establish these compounds as useful intermediates in organic synthesis. The present communication is concerned with the action of alkylmagnesium halides

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on α -lactams, a novel insertion-type alkylation of acyl groups.

To a stirring solution of methylmagnesium iodide (obtained from methyl iodide, 710 mg, and triply sublimed magnesium, 120 mg, in 15 ml of diethyl ether) was added a solution of 1,3-di-t-butylaziridinone,6 845 mg in 10 ml of diethyl ether at 0°. After 3 hr at room temperature the mixture was hydrolyzed (ammonium chloride-water) to give 740 mg of a crystalline solid, mp 96-97°, with the empirical formula⁷ $C_{11}H_{23}NO$. The infrared absorption (KBr disk), 3200, 1655, and 1540 cm^{-1} , shows the presence of the -CONH- group. The nmr spectrum (CDCl₃), 350 (broad, 1 H), 130 (triplet, 2 H), 79 (singlet, 9 H), 116 (triplet, 2 H), and 60 Hz (singlet, 9 H), suggests two t-butyl groups and a -CH₂CH₂- moiety. The mass spectrum of the compound shows m/e at 185 mu and contains a peak at m/e 129 mu (60%) from the loss of C₄H₈, as indicated in the structure below.^{8,9} On the basis of this infor-



mation, the compound was assigned the structure N-*t*-butyl-4,4-dimethylvaleramide (VIa).

In a similar manner ethylmagnesium bromide with α -lactams Ia produced N-*t*-butyl-2,4,4-trimethylvaleramide VIb: mp 107°; ir (KBr disk), 3210, 1650, and 1545 cm⁻¹; nmr (CDCl₈), 320 (broad, 1 H), 131 (multiplet, 1 H), 118 (doublet, 2 H), 80 (singlet, 9 H), 60 (singlet, 9 H), and 58 Hz (doublet, 3 H); mass spectrum, m/e 199 and had no peak at M – 28, which indicates the absence of an α -ethyl group with respect to carbonyl necessary to undergo 1,6-hydrogen transfer.⁹



The reaction between ethylmagnesium bromide and 1-t-butyl-3-(1-methylcyclopentyl)aziridinone (Ic) and 1-t-butyl-3-(1-methylcyclohexyl)aziridinone (Id)¹ were also studied; similar results were obtained.

Scheme I represents a possible path for the formation of rearranged product from the reaction between alkylmagnesium halides and α -lactams. The first step was assumed to be the addition of the Grignard reagents to form the amino ketals II followed by elimination to give a methylenaziridine, III, which rearranged to a cyclopropylidenimine, IV. The interconversion of methylenaziridine to cyclopropylidenimine has been reported by Deyrup and Greenwald¹⁰ and is similar to the recently reported allene oxidecyclopropanone rearrangement.¹¹ These types of re-

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arrangements of three-membered cyclic compounds containing one sp²-hybridized carbon atom in the ring are well documented.¹² The hydrolytic ring opening of cyclopropylidenimine is controlled sterically, and in the present case path a is more favorable.

Scheme I



a,
$$R = R' = (CH_3)_3C$$
; $R'' = H$; $X = I$
b, $R = R' = (CH_3)_3C$; $R'' = CH_3$; $X = Br$
c, $R = \bigcirc CH_3$
; $R' = (CH_3)_3C$; $R'' = CH_3$; $X = Br$
d, $R = \bigcirc CH_3$
; $R' = (CH_3)_3C$; $R'' = CH_3$; $X = Br$

The action of alkylmagnesium halide on α -lactams has not been reported previously, and the present results open a new route for insertion-type alkylation to achieve organic molecules with a higher number of carbon atoms in the chain as well as selective side chains.

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