Formolysis of Cyclopent-3-enyl-d_6 Tosylate. Cyclopent-3-enyl-*1,2,2,3,4,*(cis-*5*)-d_6 tosylate (0.119 g, 0.005 mol) and sodium formate (0.0371 g, 0.00056 mol) were dissilved in 5 mL of formic acid (solution 0.1 M in tosylate). The solution was placed in a glass tube and sealed under N_2. The temperature was held at 35 °C for 12 h by means of a constant-temperature bath. The solution was cooled, washed with brine, and extracted with 5 × 10 mL of diethyl ether. The organic portions were washed with saturated $NaHCO_3$ solutions and dried ($MgSO_4$). The ether was removed by careful fractional distillation.

Hydrolysis of Cyclopent-3-enyl-d_6 Tosylate. Cyclopent-3-enyl-*1,2,2,3,4,*(*cis-5*)-d_6 tosylate (0.244 g, 0.001 mol) and 2,6-lutidine (0.214 g, 0.002 mol) were dissolved in enough 70% 1,4-dioxane/water to make 10 mL (0.1 M in tosylate). The solution was placed in glass tube and sealed under N_2. The temperature was held at 70 °C for 24 h by means of a constant-temperature bath. The reaction mixture was cooled, poured into H_2O, and extracted with diethyl ether. The organic portions were washed with ice-cold 10% HCl, saturated aqueous $NaHCO_3$, and saturated NaCl. The ether was dried (K_2CO_3) and removed by careful distillation through a Vigreux column.

Registry No. Cyclopentadiene, 542-92-7; cyclopentadiene-d_6, 2102-16-1; cyclopent-3-enol-*1,2,2,3,4,*(*cis-5*)-d_6, 84752-75-0; cyclopent-3-enyl-*1,2,2,3,4,*(*cis-5*)-d_6 tosylate, 74260-25-6; cyclopent-3-enyl-*1,2,2,3,4,*(*cis-5*)-d_6 formate, 74260-26-7; cyclopent-3-enyl-*1,2,2,3,4,*(*cis-5*)-d_6 acetate, 84774-92-5; cyclopentyl brosylate, 4596-40-1; cyclopent-3-enyl tosylate, 36367-85-8; cyclohexyl tosylate, 953-91-3; cyclohex-3-enyl tosylate, 26431-20-9.

Photochemical Reactions of α-Oxo Amides. Norrish Type II Reactions via Zwitterionic Intermediates

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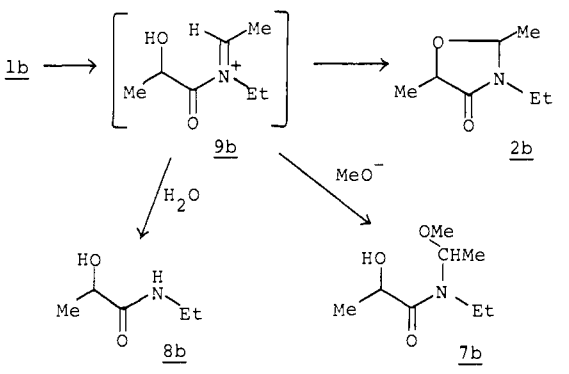
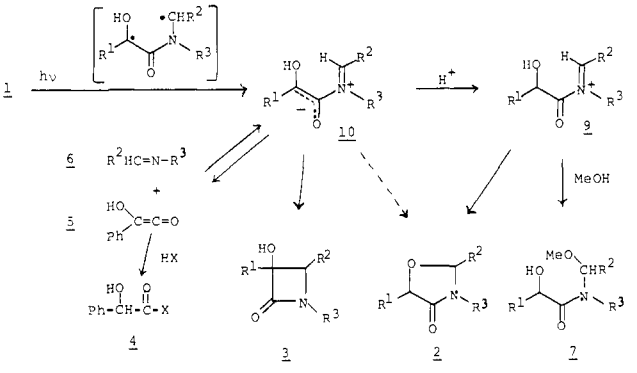
Abstract: The mechanism of the photochemical reactions of α-oxo amides was studied. Establishment of the intermediacy of zwitterions was accomplished by the detection of iminium ions formed by protonation of the zwitterions and by the independent generation of the zwitterions by the reaction of hydroxyphenylketene with imines. The remarkable substituent and solvent effects in the photoreactions were rationalized on the basis of the mechanism.

The photochemistry of α-oxo amides has received much attention because of the synthetic utilities,[1-6] and is of interest also mechanistically since α-dicarbonyl compounds show considerably different photochemical behavior from that of monoketones.[7] Photolysis of N,N-disubstituted α-oxo amides gives three types of products, oxazolidin-4-ones (**2**), β-lactams (**3**), and hydroxyketene-derived products, mandelic acid derivatives (**4**).[1,3a] The formation of these products has been explained in terms of 1,4-diradical intermediates formed by γ-hydrogen abstraction (type II photoprocesses).[1-6] However, the photoreactions show remarkable solvent and substituent effects which are not easily explained by the diradical mechanism.[3a] We have investigated the mechanism of the photoreactions and clarified that the intermediates are zwitterions. Intermediacy of 1,4-diradicals in usual type II reactions is well established.[8] The photochemical reactions of α-oxo amides provide the first example of type II reactions which involve zwitterionic intermediates. The solvent and substituent effects are also discussed in this paper.

Scheme I



Scheme II



Results and Discussions

α-Oxo amides chosen in this mechanistic study are shown in Figure 1. Since photoreactions of some α-oxo amides in aprotic solvents are sensitive to moisture and the reproducibilities of these reactions are not always good, the present study is mainly con-

(1) (a) Åkermark, B.; Johanson, N. G.; Sjöberg, B.; *Tetrahedron Lett.* **1969**, 371. (b) Johanson, N. G.; Åkermark, B.; Sjöberg, B. *Acta Chem. Scand., Ser. B* **1976**, *B30*, 383.

(2) Henery-logan, K. R.; Chen, C. G. *Tetrahedron Lett.* **1973**, 1103.

(3) (a) Aoyama, H.; Hasegawa, T.; Watabe, M.; Shiraishi, H.; Omote, Y. *J. Org. Chem.* **1978**, *43*, 419. (b) Aoyama, H.; Hasegawa, T.; Omote, Y. *J. Am. Chem. Soc.* **1979**, *101*, 5343. (c) Aoyama, H.; Sakamoto, M.; Omote, Y. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1357.

(4) Zehavi, U. *J. Org. Chem.* **1977**, *42*, 2821.

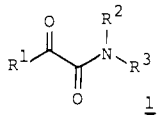
(5) Shiozaki, K.; Hiraoka, T.; *Synth. Commun.* **1979**, *9*, 179.

(6) Shima, K.; Furukawa, S.; Tanabe, K. 40th Annual Meeting of the Chemical Society of Japan, October, 1979, Fukuoka. They reported that photolysis of **1a** gave **2a**, **7a**, and an unidentified product in a ratio, 24:55:21.

(7) For photochemical reactions of α-diketones, see: (a) Wagner, P. J.; Zepp, R. G.; Liu, K.; Thomas, M.; Lee, T.; Turro, N. J. *J. Am. Chem. Soc.* **1976**, *98*, 8125 and references cited therein. For those of α-oxo esters, see: (b) Hammond, G. S.; Leermakers, P. A.; Turro, N. J. *Ibid.* **1961**, *83*, 2395. (c) Huyser, E. S.; Neckers, D. C. *J. Org. Chem.* **1964**, *29*, 276. (d) Leermakers, P. A.; Ross, M. E.; Vesley, G. F.; Warren, P. C. *Ibid.* **1965**, *30*, 914 and references cited therein. For those of α-oxo acids, see: (e) Vesley, G. F.; Leermakers, P. A. *J. Phys. Chem.* **1964**, *68*, 2364 and references cited therein. For those of α-oxoacid imides, see: (f) Aoyama, H.; Sakamoto, M.; Omote, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 119.

(8) (a) Wagner, P. J.; Kelso, P. A.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7480. (b) Wagner, P. J.; Liu, K.; Noguchi, Y. *Ibid.* **1981**, *103*, 3837. (c) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *50*, 431. (d) Kaptein, R.; de Kanter, F. J. J.; Rist, G. H. *J. Chem. Soc., Chem. Commun.* **1981**, 499.

0002-7863/83/1505-1958$01.50/0



1

a: $R^1=R^2=R^3=Me$ h: $R^1=Ph$, $R^2=R^3=Pr^i$

b: $R^1=Me$, $R^2=R^3=Et$ i: $R^1=Ph$, $R^2=R^3=C_6H_5CH_2$

c: $R^1=Me$, $R^2=R^3=Pr^i$ j: $R^1=R^2=Ph$, $R^3=Et$

d: $R^1=Me$, $R^2=R^3=C_6H_5CH_2$ k: $R^1=R^2=Ph$, $R^3=Pr^i$

e: $R^1=Me$, $R^2=R^3=p\text{-}CNC_6H_4CH_2$

f: $R^1=Me$, $R^2=R^3=p\text{-}MeOC_6H_4CH_2$

g: $R^1=R^2=Me$, $R^3=1\text{-adamantyl}$

Figure 1.

Table I. Photolysis of 1b in the Presence of Nucleophiles

reaction medium	yields,[a] % 2b	7b	8b
MeOH	~100	*b*	
MeOH-MeONa (0.10 M)	47	50	
MeOH-MeONa (0.02 M)	52	46	
MeOH-H_2O (5%)	~100	*b*	
MeOH-H_2O (50%)	78	18	

[a] Determined by NMR spectroscopy. [b] Not detected.

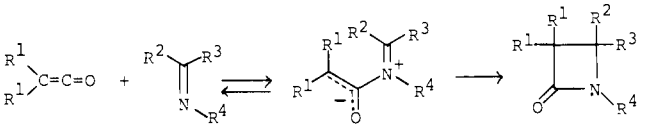
cerned with the photoreactions in protic solvents.

Intermediacy of Iminium Ions in the Formation of Oxazolidin-4-ones (2). Shima et al. reported that irradiation of *N,N*-dimethylpyruvamide (**1a**) in methanol gave a methanol adduct (**7a**), and an iminium ion (**9a**) was presumed to be an intermediate[6] (Scheme II). In the previous paper,[3c] we suggested a possibility that oxazolidinones (**2**) are produced by cyclization of the iminium ions (**9**). A similar cyclization of an iminium ion produced by electrolysis of a carbamate bearing a hydroxy group was reported.[9]

In order to examine the intermediacy of the iminium ion (**9**), we tried trapping the ion with strong nucleophiles. Photolysis of *N,N*-diethylpyruvamide (**1b**) in methanol does not give a methanol adduct but affords an oxazolidinone (**2b**) quantitatively.[3a] However, irradiation of **1b** in methanol containing sodium methoxide yielded the methanol adduct (**7b**) as a main product accompanied by **2b** (Scheme I). The ratio of the two products was dependent on the concentration of sodium methoxide (Table I). The formation of the adduct strongly indicates that the iminium ion (**9b**) is the intermediate of the reaction. When **1b** was photolyzed in aqueous methanol, *N*-ethyllactamide (**8b**) was obtained in addition to **2b**. The formation of **8b** is also consistent with the mechanism since hydrolysis of **9b** would give **8b**. The observation that **2b** is stable in these reaction conditions rules out the possibility that **7b** and **8b** are formed from **2b** as secondary products. On the basis of these facts, we can conclude that the iminium ion (**9**) is the intermediate in the formation of the oxazolidinone (**2**).

It is quite difficult to explain the formation of the iminium ion in terms of the diradical mechanism, whereas the formation is reasonably explained by protonation of a zwitterion (**10**) (Scheme II) (for the relation between zwitterions and diradicals, see the following section). Furthermore, the formation of other products (**3** and **4**) in the photoreaction of α-oxo amides can be rationalized by the mechanism involving the zwitterionic intermediate (Scheme II). It is known that β-lactams are formed from zwitterions produced by addition of ketenes with imines (Scheme III).[10,11]

Scheme III



Scheme IV

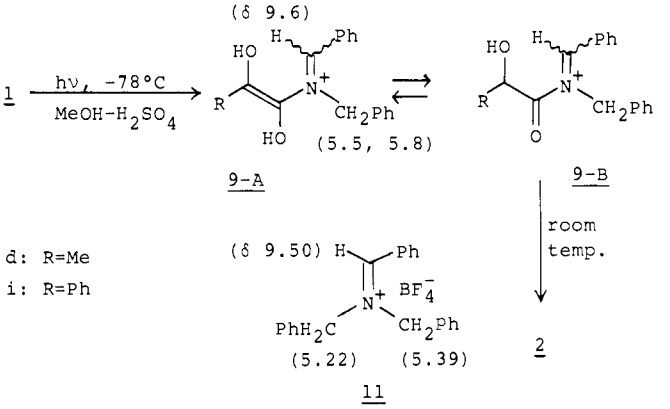


Table II. Photolysis of 1d and 1i in the Presence of Acids or Bases

reactant	reaction medium	yields, % 2	3
1d	C_6H_6	*a*	94
	MeOH[c]	43	54
	MeOH-AcOH (5%)	84	*b*
	MeOH-MeONa (0.1 M)	*a*	87
1i	C_6H_6	*a*	~100
	MeOH	*a*	86
	MeOH-H_2SO_4 (10%)	51	24

[a] Not detected. [b] Trace. [c] Reference 13.

Cleavage of the zwitterions to ketenes and imines is also known.[12]

Effects of Acids and Bases. According to the mechanism shown in Scheme II, the oxazolidinone (**2**) is formed from the iminium ion (**9**) which is produced by protonation of the zwitterion (**10**), while the β-lactam is formed directly from **10**. If the mechanism is correct, the concentration of acids should play a crucial role in the photoreaction in which the oxazolidinone and the β-lactam are formed competitively. Accordingly, photolyses of α-oxo amides (**1d** and **1i**) in the presence of acids or bases were carried out and the results are summarized in Table II. The presence of acids in the reaction media apparently enhances the formation of **2**, and the β-lactam (**3**) becomes favored in basic or aprotic media. In particular, *N,N*-dibenzylbenzoylformamide (**1i**) which gives only a β-lactam (**3i**) in both protic and aprotic solvents yields an oxazolidinone (**2i**) as a main product on irradiation in a highly acidic medium. These results strongly support the mechanism involving the zwitterion and are inconsistent with the diradical mechanism since it is quite unlikely that diradical reactions are affected by acids and bases so remarkably.

Detection of Iminium Ions. Attempts to detect the zwitterions (**10**) by use of low-temperature NMR spectroscopy met with failure.[14] This is presumably due to instability of the intermediates. It is conceivable that the iminium ions produced by

(9) Shono, T.; Hamaguchi, H.; Matsumura, Y. *J. Am. Chem. Soc.* **1975**, *97*, 4264.

(10) Huisgen, R.; Davis, B. A.; Morikawa, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 826.

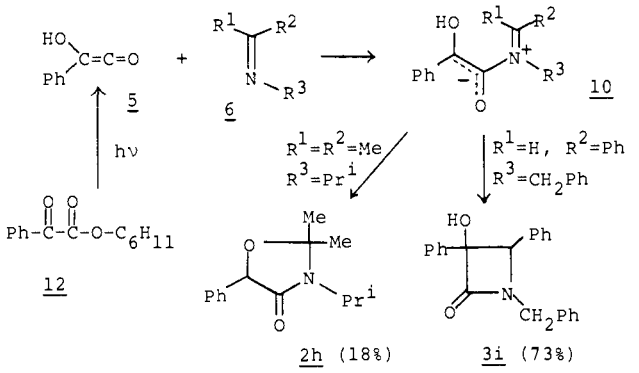
(11) (a) Gomes, A.; Joullie, M. M. *Chem. Commun.* **1967**, 935. (b) Kagan, H. B.; Luche, J. L. *Tetrahedron Lett.* **1968**, 3093. (c) Martin, J. C.; Brannock, K. C.; Burpitt, R. D.; Gott, P. G.; Hoyle, V. A., Jr. *J. Org. Chem.* **1971**, *36*, 2211.

(12) (a) Moore, H. W.; Hernandes, L., Jr.; Kunert, D. M.; Mercer, F.; Sing, A. *J. Am. Chem. Soc.* **1981**, *103*, 1769. (b) Moore, H. W.; Wilbur, D. S. *J. Org. Chem.* **1980**, *45*, 4483. (c) Moore, H. W.; Gheorghiu, M. D. *Chem. Soc. Rev.* **1981**, 289.

(13) In the previous paper,[3a] we reported that photolysis of **1d** in methanol gave **2d** (78%) and **3d** (17%). However, the experiments repeated carefully showed that the yields are those shown in Table II. The higher yield of **2d** in the previous experiment might be due to acidic impurities, since the photoreaction of **1d** is sensitive to acids (see the text).

(14) Recently, detection of zwitterions (**14**) (Scheme VII) was reported: Pacansky, J.; Chang, J. S.; Brown, D. W.; Schwarz, W. *J. Org. Chem.* **1982**, *47*, 2233. The ions are relatively stable because the cyclization requires the destruction of the aromaticity of the imidazole ring.

Scheme V



protonation of the zwitterions are more stable. Thus, detection of the iminium ions (**9**) was examined. When the oxoamide (**1i**) in methanol containing sulfuric acid (5%) was irradiated at −78 °C, the solution turned reddish brown (Scheme IV). On warming to −10 °C, the solution rapidly became colorless again. This indicates the formation of an unstable intermediate. Similar phenomena occurred in the case of other acids, but were not observed when acids were absent. When a weak acid, acetic acid, was used, decoloration of the irradiated solution took place at a lower temperature (−50 °C). From these facts, it is evident that the unstable compound is a protonated species. The visible spectrum of the cold reaction mixture exhibited a maximum absorption at 440 nm, which disappeared rapidly on warming. The NMR spectrum of the mixture was measured at −50 °C. The spectrum showed signals at δ 9.6, 5.5, and 5.8 as broad singlets[15] in addition to those of the original amide. The three signals disappeared when the spectrum was measured after the mixture warmed to room temperature, and the signals of the oxazolidinone (**2i**) appeared instead. These results clearly show that the unstable protonated species is converted into **2i** on warming. This fact and the comparison of the chemical shifts of the three signals with those of a known iminium ion (**11**)[16] (Scheme IV) strongly indicate that the intermediate is an iminium ion (**9i**). Since the ion showed an absorption at a long wavelength region, it is presumed to exist predominantly in the enol form (**9i**-A) rather than the keto form (**9i-B**) in these conditions.

A similar phenomenon was observed when the pyruvamide (**1d**) was irradiated under the same conditions. However, the NMR spectrum of the intermediate of this reaction could not be measured because its lifetime was short even at the low temperature. The visible spectrum of the reaction mixture showed a maximum absorption at 416 nm. This value is considerably smaller than that in the case of **1i**. This difference is also compatible with the enol structure (**9**-A) in which the phenyl group of **9i** or the methyl group of **9d** is directly bonded to the conjugated system. Meanwhile, in spite of the preponderant presence of the enol form (**9**-A) in the cold reaction mixtures, the cyclization of **9** to **2** is presumed to occur from the keto form (**9**-B) (Scheme IV) as detailed in the following section.

On the basis of these results, we can safely conclude that the unstable intermediates are iminium ions (**9i** and **9d**), and they undergo cyclization to yield the oxazolidinone, **2i** and **2d**, respectively. On the other hand, when α-oxo amides (**1b**,**c**,**h**) were irradiated under the same conditions, no intermediates were detected. The iminium ions from these amides presumably undergo cyclization rapidly to give the corresponding oxazolidinones even at the low temperature.

Independent Generation of the Zwitterions by the Reaction of Hydroxyphenylketene with Imines. It is well-known that the reaction of ketenes with imines yields zwitterions (Scheme III). Therefore, the reaction of hydroxyketenes with imines should give the zwitterions which are identical with those formed in the photolysis of α-oxoamides. Hydroxyketenes do not exist as stable compounds because they readily ketonize to α-oxo aldehydes. However, it is known that hydroxyphenylketene (**5**) is formed in the photolysis of benzoylformic acid esters and it can be trapped by nucleophiles such as alcohols.[7c] Thus the photolysis of cyclohexyl benzoylformate (**12**) in the presence of imines was carried out (Scheme V). When a 1:1 mixture of **12** and *N*-benzylidenebenzylamine in dry benzene was photolyzed, the β-lactam (**3i**) was obtained in a good yield as expected. Furthermore, an oxazolidinone (**2h**) was obtained in the case of *N*-isopropylideneisopropylamine. These products and the substituent effects fully correspond with those in the photolysis of the α-oxo amides (**1i** and **1h**): irradiation of **1i** in benzene gives **3i** quantitatively and that of **1h** affords **2h** as a main product.[3a] From these results it is apparent that the photoproducts (**2** and **3**) arise from the zwitterion (**10**).

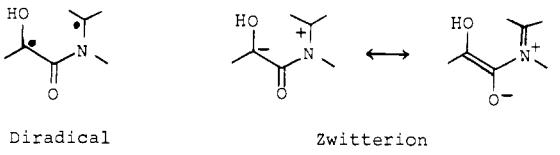


Figure 2.

It may be conceivable that the ketene (**5**) and the imine (**6**) are formed initially in the photolysis of **1** by a usual type II cleavage of **1** and the oxazolidinone (**2**) and the β-lactam (**3**) are produced from the ketene–imine pair via the zwitterion as secondary products. However, this mechanism is improbable because the amide (**1c** and **1i**) gave **2c** and **3i**, respectively, almost quantitatively on irradiation in *n*-butylamine which is a stronger nucleophile than imines. These facts lead to the conclusion that the intermediates in the photoreaction of α-oxo amides are zwitterions (**10**) as shown in Scheme II.

Diradicals and Zwitterions. The problems of diradicals and zwitterions have already been discussed extensively by Salem, Turro, and Dauben.[17] In the case of nonsymmetric singlet diradicals (or zwitterions), the diradical and zwitterionic structures (e.g., those shown in Figure 2) are resonance forms. Namely, the states of these diradicals or zwitterions can be represented by linear combinations of diradical (covalent) terms and zwitterionic terms. The relative weights of the contributing structures are determined by the substituents, geometries, and environmental effects. Thus, the terms "singlet diradical" and "zwitterion" are only simplifications of the real situation.[17a] Nevertheless, when contribution of the diradical structures is much larger than that of the zwitterionic ones, we can regard the species as diradicals as in the case of diradicals produced in singlet type II reactions, whereas the species can be regarded as zwitterions in the reverse case (e.g., intermediates in the thermal 2 + 2 cycloaddition of electron-rich olefins with electron-poor olefins).[18] When the lowest singlet state of a species is a diradical state, the second singlet state (the lowest excited singlet state) is a zwitterionic state, and vice versa.[17a] On the other hand, it is worth emphasizing that triplet diradicals can not have zwitterionic characters.[17a,c] The states of triplet diradicals are represented only by covalent terms.

Usually, the triplet and singlet diradical states lie below the zwitterionic state. However, when the zwitterionic state is strongly stabilized by appropriate substitution, it falls below the two diradical states and becomes the ground state of the system. In the present case, the zwitterion (**10**) is undoubtedly the ground state of the system because it can be produced by the ground-state reaction of the ketene and imine. The cationic center of **10** is conjugated with the nitrogen and the anionic center is conjugated with the adjacent carbonyl group (Figure 2). The zwitterionic state is thus stabilized by the conjugation and becomes the ground state. The most stable geometry of the zwitterion (**10**) should

(15) The broadening of the signals is apparently due to the viscosity of the cold solution.

(16) Smith, P. A. S.; Leoppky, R. N. *J. Am. Chem. Soc.* **1967**, *89*, 1147.

(17) (a) Salem, L.; Rowland, C. *Angew Chem., Int. Ed. Engl.* **1972**, *11*, 92. (b) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978. (c) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41.

(18) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 199, 117.

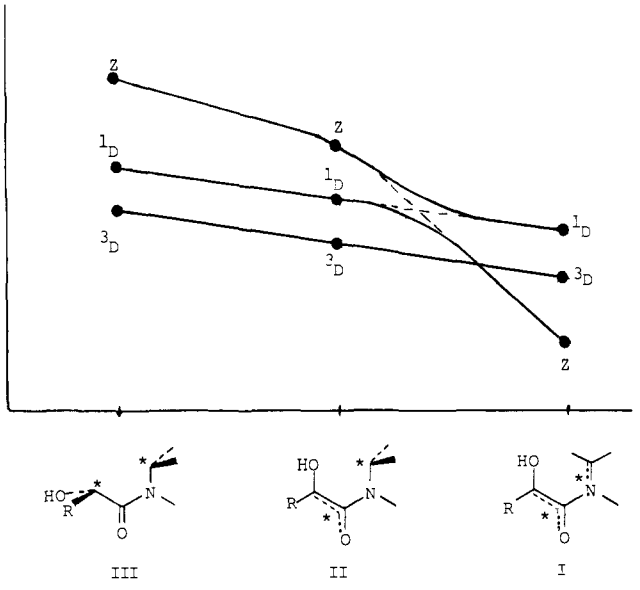
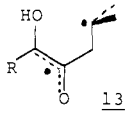


Figure 3. Qualitative potential energy diagram for geometrical changes of **10** (*,* = +,− or ·,·).



13

Figure 4.

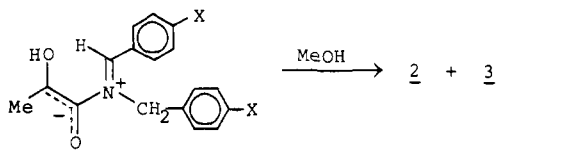
be nearly planar because of the conjugation.[19]

The energies of zwitterionic and diradical states are dependent on the geometry of the system.[17] Figure 3 shows the qualitative potential energy surfaces for geometrical changes of the system, and three typical geometries are shown in it. The ground state of the planar conformer I is zwitterionic as described above. In the case of the partially twisted geometry II, conjugation of the cationic center with the nitrogen is completely forbidden. Therefore, the zwitterionic state is strongly destabilized and the diradical state is presumed to become the ground state of this conformer. This diradical is closely similar to the diradical (**13**) formed in the type II reaction of α-diketones (Figure 4).[7a]

The ground state of the fully twisted conformer III is undoubtedly the diradical state because stabilization of the zwitterionic state is not expected in this geometry. From this diradical, the β-lactam can be smoothly formed. However, the geometry of the transition state in the formation of the β-lactam is not this geometry because the bond formation and the bond rotation should occur simultaneously in the cyclization.[20] Nevertheless, the transition state should have a partial diradical character, as in the case of butadiene–cyclobutene electrocyclization,[21] because the geometry of the transition state should be severely distorted from the planar structure.

Multiplicities of the Reactive Excited States and the Intermediates. The photochemical reactions of α-oxo amides are sensitizable but unquenchable.[3a] The failure to quench the reactions makes it impossible to achieve the usual kinetic studies and difficult to determine the multiplicities of the reactive excited states in the direct photolysis because both singlet and rapid triplet reactions are possible from the available data. In the case of sensitized reactions, triplet diradicals should be formed initially since triplet states cannot be zwitterionic as described above. The potential energy surface of the triplet diradical is presumed to lie below

Scheme VI



10 d: X=H e: X=CN f: X=OMe

Table III. Photolysis of *N,N*-Dibenzylpyruvamide Derivatives in Methanol[a]

reactant	yields, % 2	3
1d	43	54
1e	*b* (0)	86 (92)
1f	67 (0)	21 (96)

[a] Numbers in parentheses are the yields of the photolysis in benzene. [b] Trace.

that of the singlet diradical (Figure 3) as in the case of usual diradicals. The triplet surface should cross the singlet surface in the region where the lowest singlet state begins to have a zwitterionic character and is strongly stabilized. The triplet diradical must undergo intersystem crossing to the singlet state before it undergoes further reactions, and the efficient intersystem crossing is expected to occur in the crossing region (Figure 3).

Xanthone-sensitized photolysis[22] of **1b** in methanol and **1d** in methanol containing acetic acid (5%) gave **2b** (~100%) and **2d** (86%), respectively. The yields are almost the same as those in the direct photolysis. This indicates that the triplet diradicals formed in the sensitized reactions are eventually converted to the zwitterions exclusively, since it is sure that the oxazolidinones (**2**) are produced from the zwitterions (**10**). In particular, the fact that the formation of the β-lactam from **1d** was completely suppressed by the addition of acetic acid even in the sensitized reaction indicates that the direct formation of the β-lactam from the triplet diradical[23] is negligible at least in the case of **1d**. On the basis of these results, the triplet diradicals formed in the sensitized photoreacitons of α-oxo amides are presumed to undergo rapid intersystem crossing and to be converted to the zwitterions (**10**). Meanwhile, **10** might be formed directly from the singlet excited state of **1** in case of the direct photolysis, since the singlet diradical from **1** may not represent energy minima in the potential energy surface (Figure 3) even if it is produced in the photolysis.

Substituent Effects. Photochemical reactions of α-oxo amides show substantial substituent effects.[3a] They are now reasonably explained in terms of the mechanism described in the preceding sections.

1. β-Lactams vs. Oxazolidinones. Radical-stabilizing substituents apparently enhance the formation of β-lactams: *N,N*-dibenzylbenzoylformamide (**1i**) gives the β-lactams (**3i**) as a sole product both in protic and aprotic solvents, and *N,N*-dialkylpyruvamides (**1b** and **1c**) afford only oxazolidinones (**2b** and **2c**), respectively, whereas **1d** and **1h** yield both β-lactams (**3**) and oxazolidinones (**2**).[3a] Similar substituent effects are known. With few exceptions, the formation of β-lactams from ketenes and imines has been limited to imines which have aromatic groups at the imino carbons (Scheme III, R^2 and/or R^3 is aryl).[11c] The radical-stabilizing phenyl groups at the radical (or ionic) center of **10** should lower the potential energies of the transition states in the formation of the β-lactams because the transition states have partial diradical

(19) Moore et al. also assumed the planar structures for the zwitterions closely similar to **10** (ref 12b).

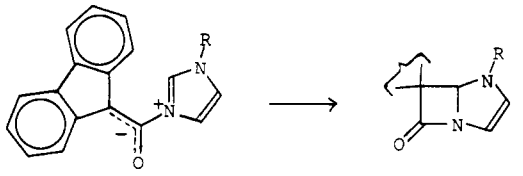
(20) Moore et al. explained the stereospecificity in the cyclization of zwitterions closely similar to **10** in terms of a concerted conrotatory ring closure (ref 12a,b).

(21) Houk, K. N. "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; p 246.

(22) The triplet and singlet energies are as follows. Xanthone: E_T = 74 kcal, E_S = 77.6 kcal (Murov, S. L. "Handbook of Photochemistry"; Mercel Dekker: New York, 1973). *N,N*-Dialkylpyruvamides: 65 kcal < E_T < 72 kcal (estimated from the photoreactions using various sensitizers). Pyruvamide: E_T = ~67 kcal, E_S = ~79 kcal (Larson, D. B.; Arnet, J. F.; Seliskar, C. J.; McGlynn, S. P. *J. Am. Chem. Soc.* **1974**, *96*, 3370).

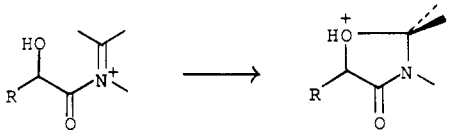
(23) This process is possible if the triplet diradical undergoes intersystem crossing to the singlet state at the geometry which is located after the transition state in the reaction (**10** → **3**) coordinate.

Scheme VII



14 15

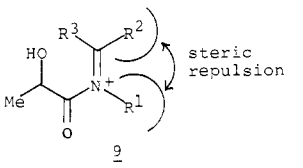
Scheme VIII



characters as described in the preceding section. Thus, the stabilization of the transition states make the cyclization efficient.

The activation energy of the cyclization is dependent not only on the potential energy of the transition state but also on that of the zwitterion (**10**). Therefore, it is presumed that stabilization or destabilization of **10** shows substantial effects on the photoreaction **1**. In confirmation of this, photolysis of *N*,*N*-dibenzylpyruvamide derivatives was examined (Scheme VI and Table III). As expected, introduction of cyano groups to the phenyl groups increased the yield of the β-lactam (**3e**) and that of methoxy groups decreased the yield (**3f**). The electron-withdrawing group at the cationic center should destabilize **10e**. Raising the potential energy of the zwitterion makes the activation energy small and thus enhances the formation of the β-lactam. The reverse is true for the electron-donating methoxy group since the stabilization of the zwitterion by the methoxy group should make the activation energy large. Quite analogous substituent effects were recently reported.[14] The rate of cyclization of a zwitterion (**14**) to a β-lactam (**15**) becomes fast when electron-withdrawing groups are introduced at the 1-position of the imidazole ring (Scheme VII). These facts are also consistent with the above explanation.

2. Oxazolidinones vs. Methanol Adducts. The oxazolidinone (**2**) and the methanol adduct (**7**) are formed from the iminium ion (**9**) competitively as shown in Scheme II. Among pyruvamides, only the *N*,*N*-dimethylamide (**1a**) affords the methanol adduct (**7a**) on irradiation in methanol.[6] The *N*,*N*-diethylamide (**1b**) gives the adduct (**7b**) only when sodium methoxide is present (vide supra). Meanwhile, the *N*,*N*-diisopropylamide (**1c**) did not yield an adduct even in the presence of sodium methoxide. Therefore, the reactivity toward the attack of methanol or methoxide ion is reduced in the series **1a** > **1b** > **1c**. This order is in accord with that of the reactivity of the corresponding iminium ions (**9**) toward nucleophiles because the electron-donating methyl groups at the imino carbon should reduce the reactivity. However, the selective intermoelcular reaction (methanol addition) of **9a** cannot be attributed to the high reactivity because the imino group of **9a** should be highly reactive toward not only intermolecular but also intramolecular nucleophilic attacks. The efficient formation of the adduct from **1a** can be rationalized in terms of steric effects as detailed below. The intramolecular cyclization of the iminium ion (**9**) requires the rotation of the C=N bond (Scheme VIII). The bulky substituents of **9b** and **9c** are presumed to destabilize the planar structure of the imino group and make the group slightly twisted (Figure 5). The twist should enhance the intramolecular reaction (oxazolidinone formation). In the case of **9a** which has no bulky substituents at the imino carbon, the intramolecular reaction is less favorable process because the imino group is planar, and the intermolecular reaction with methanol takes place selectively. In confirmation of this, photolysis of *N*-(1-adamantyl)-*N*-methylpyruvamide (**1g**) was carried out. Irradiation of **1g** in methanol gave only an oxazolidinone (**2g**) (~100%), and that of **1g** in methanol containing sodium methoxide (0.1 M)



a: R^1=Me, R^2=R^3=H
b: R^1=Et, R^2=Me, R^3=H
c: R^1=Pr^i, R^2=R^3=Me
g: R^1=1-Adamantyl, R^2=R^3=H

9

Figure 5.

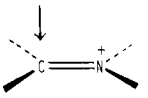


Figure 6. Direction of an effective attack of nucleophiles to imino groups.

Table IV. Photolysis of 1h, 1j, and 1k in Methanol[a]

reactant	yields, % 2	3	4
1d	58	22	16[b]
1j	11	5	36[b]
1k	16 (14)	13 (26)	69[b] (19)[c]

[a] Numbers in parentheses are yields of the photolysis in benzene. [b] Methyl mandelate. [c] Mandelanilide.

yielded both **2g** (47%) and a methanol adduct (**7g**) (48%). The less efficient formation of the adduct from **1g** than that from **1a** is consistent with the above explanation that the steric effects are more important, since the reactivity of **9g** toward the intermolecular attack by methanol should be almost the same as that of **9a** and the bulky adamantyl group should destabilize the planar structure of the imino group of **9g**.

3. Photoeliminations. None of the pyruvamides chosen in this investigation undergo photoeliminations. Among benzoylformamides, only *N*,*N*-diisopropylamide (**1h**) and anilides (**1j** and **1k**) gave the elimination products, mandelic acid derivatives (**4**) (see Table IV). The formation of the oxazolidinone (**2h**) from hydroxyphenylketene (**5**) and the imine (**6h**) (Scheme V) clearly shows that the elimination of the zwitterion (**10h**) is reversible[12] (Scheme II). The formation of the elimination product in the photolysis of **1h** is not unreasonable since the steric congestion due to the bulky substituents should enhance the elimination. In the case of the anilides, the stabilization of the anils (**6j** and **6k**) due to the conjugation of the C=N bond with the phenyl group may be responsible for the efficient elimination; this conjugation is presumed to be stronger than that in the zwitterion (**10j** and **10k**) because the steric congestion in **6** must be smaller than that in **10**. Thus, the anilide (**1k**) which possesses a bulky alkyl group gave the elimination product, methyl mandelate, in a high yield on irradiation in methanol.

Solvent Effects. The effects of acids and protic solvents on the photoreactions of α-oxo amides were already described in the preceding section in relation to the mechanism of the reactions. Although protic solvents enhance the formation of the oxazolidinones (**2**), some α-oxo amides (e.g., most of dialkylpyruvamides and **1h**) yield the corresponding oxazolidinones even in aprotic solvents.[3a] Therefore, the direct formation of **2** from the zwitterion (**10**) is presumed to occur in these conditions. However, most of these reactions in aprotic solvents are not clean and the yields of **2** are low. Furthermore, addition of small amounts of protic substances such as alcohols or water to the aprotic solvents significantly increase the yields of **2**.[3a] These facts and the efficient formation of **2** in acidic media (vide supra) indicate that the direct formation of **2** from **10** is not a favorable process and the formation of **2** in protic solvents proceeds mainly from the iminium ion (**9**) as shown in Scheme II.

The more efficient cyclization of the iminium ions than that of the zwitterions can be rationalized in terms of stereoelectronic requirements for the nucleophilic attacks to imino groups. The effective attacks of nucleophiles to the imino carbon of iminium ions should be those from the directions nearly orthogonal to the imino plane (Figure 6) as in the case of nucleophilic attacks to

Table V. Photolysis of 1d in Various Solvents

solvents	yields, % 2d	3d
C_6H_6	*a*	94
THF	*a*	93
MeCN	*a*	96
MeOH	43	54
i-PrOH	22	63

[a] Not detected.

carbonyl groups.[24] The hydroxy group of the zwitterion (**10**) or the enol form of the iminium ion (**9-A**) (Scheme IV) cannot undergo such attacks without distorting the planar structure of the imino group or the enol moiety, whereas the geometry of the keto form of the iminium ion (**9-B**) is much more suitable for the intramolecular attack because of the tetrahedral structure of the carbon bearing the hydroxy group. Therefore, the formation of **2** from the iminium ion is presumed to occur preferably from the keto form (**9-B**) (Scheme IV).

In contrast to the remarkable effects of protic substances, solvent polarities showed little effects on the photoreaction of **1d** as shown in Table V.

Conclusion

Photochemical reactions of α-oxo amides (**1**) were proved to proceed via zwitterionic intermediates (**10**). The remarkable substituent and solvent effects can be rationalized on the basis of the mechanism involving **10**. The photocyclization of **1** which yields the β-lactam (**3**) and the photoelimination which affords the hydroxyketene (**5**) and imine (**6**) can be regarded as Norrish type II reactions, because the former involves γ-hydrogen abstraction by the excited carbonyl group followed by cyclization to give the four-membered cyclic compound (**3**), and the latter involves the hydrogen abstraction and subsequent cleavage of the β bond. Therefore, these reactions provide the first example of type II reactions involving zwitterionic intermediates.

Zwitterions analogous to **10** were first reported by Huisgen et al. as intermediates in the reaction of ketenes with imines.[10] Recently, Moore et al. reported the formation of the zwitterionic intermediates in the thermolysis or photolysis of 4-azido-2-pyrrolinones.[12] Therefore, the present reaction affords a novel entry to the structurally interesting and synthetically important zwitterions.

Experimental Section

Melting points are uncorrected. Yields are isolated yields unless otherwise indicated. Infrared spectra were recorded on a JASCO IRA-1 infrared spectrometer, and NMR spectra were measured on a JEOL-100 spectrometer. Visible spectra were obtained on a Shimadzu UV-365 spectrometer.

Materials. The α-oxo amides (**1b–k**) were prepared from α-oxo acid chlorides[25] and amines according to the literature.[1,3a]

***N*,*N*-Di-*p*-cyanobenzylpyruvamide (1e)**: mp 147–149 °C; IR (KBr) 2230, 1705, and 1620 cm^{-1}; NMR ($CDCl_3$) δ 2.47 (s, 3 H, Me), 4.53 (s, 4 H, CH_2), 7.2–7.7 (m, 8 H, aromatic protons).

Anal. Calcd for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.60; H, 4.68; N, 13.18.

***N*,*N*-Di-*p*-methoxybenzylpyruvamide (1f)**: mp 50–51 °C; IR ($CHCl_3$) 1710 and 1630 cm^{-1}; NMR ($CDCl_3$) δ 2.36 (s, 3 H, COMe), 3.80 (s, 6 H, OMe), 4.30 and 4.45 (two s, 4 H, CH_2), 6.75–7.8 (m, 8 H, aromoatic protons).

Anal. Calcd for $C_{19}H_{21}NO_4$: C, 69.70; H, 6.46; N, 4.27. Found: C, 69.48; H, 6.53; N, 4.29.

***N*-(1-Adamantyl)-*N*-methylpyruvamide (1g)**: mp 87–89 °C; IR ($CHCl_3$) 1705 and 1635 cm^{-1}; NMR ($CDCl_3$) δ 1.73 (br s, 6 H, adamantyl), 2.17 (br s, 9 H, adamantyl), 2.35 (s, 3 H, COMe), 2.85 (s, 3 H, NMe).

Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.45; H, 8.99; N, 5.95. Found: C, 71.24; H, 9.02; N, 5.95.

***N*-Isopropylbenzoylformanilide (1k)**: mp 133–136 °C; IR ($CHCl_3$) 1680 and 1635 cm^{-1}; NMR ($CDCl_3$) δ 1.22 (d, 6 H, *J* = 7 Hz, isopropyl methyls), 5.05 (sep, 1 H, *J* = 7 Hz, NCH), 7.0–7.9 (m, 10 H, aromatic protons).

Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.25. Found: C, 76.21; H, 6.42; H, 5.19.

General Procedure for the Photochemical Reactions of α-Oxoamides. A solution of the amide (**1**) (200 mg) in a solvent (40 mL) was irradiated in a Pyrex vessel under argon with a 300-W high-pressure mercury lamp (Eikosha) in the presence or absence of the additives. After the starting material had disappeared, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (flash chromatography). In the case of the photolysis in methanol containing sodium methoxide or sulfuric acid, the solution was neutralized with acetic acid or sodium bicarbonate before removal of the solvent. The spectral data of the products **2b**, **2c**, **2d**, **2h**, **2i**, **3d**, **3h**, and **3i** are described in the previous paper.[3a] *N*-Ethyllactamide (**8b**) was identified by direct comparison with an authentic sample.[26]

***N*-Ethyl-*N*-(1-methoxyethyl)lactamide (7b)**: bp 80 °C (3 torr) (bath temperature, Kugelrohr destillation); IR ($CHCl_3$) 3440 and 1635 cm^{-1}; NMR ($CDCl_3$) δ 1.0–1.7 (9 H, 3Me), 3.24 (s, 3 H, OMe), 3.4 (m, 2 H, CH_2), 3.8 (m, 1 H, OH, D_2O exchangeable), 4.4 (m, 1 H, C*H*OH), 4.9 and 5.8 (both m, total 1 H, NCH).

Anal. Calcd for $C_8H_{17}NO_3$: C, 54.83; H, 9.77; N, 7.99. Found: C, 54.51; H, 9.70; N, 8.09.

2,5-Diphenyl-3-benzyloxazolidin-4-one (2i): mp 95–97 °C; IR ($CHCl_3$) 1695 cm^{-1}; NMR ($CDCl_3$) δ 3.60 and 4.98 (ABq, 2 H, *J* = 15 Hz, CH_2), 5.38 (d, 1 H, *J* = 2 Hz, 5-H), 5.83 (d, 1 H, *J* = 2 Hz, 2-H), 6.95–7.6 (m, 15 H, aromatic protons).

Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.21; H, 5.81; N, 4.25. Found: C, 80.50; H, 5.82; N, 4.26.

3-(*p*-Cyanobenzyl)-2-(*p*-cyanophenyl)-5-methyloxazolidin-4-one (2e): mp 196–198 °C; IR ($CHCl_3$) 2230 and 1700 cm^{-1}; NMR ($CDCl_3$) δ 1.60 (d, 3 H, *J* = 7 Hz, Me), 3.80 and 4.79 (ABq, 2 H, *J* = 16 Hz, CH_2), 4.5 (m, 1 H, 5-H), 5.75 (d, 1 H, *J* = 2 Hz, 2-H), 7.0–7.9 (m, 8 H, aromatic protons).

Anal. Calcd for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.90; H, 4.77; N, 13.20.

1-(*p*-Cyanobenzyl)-4-(*p*-cyanophenyl)-3-hydroxy-3-methylazetidin-2-one (3e): 141–147 °C; IR ($CHCl_3$) 3320, 2235, and 1740 cm^{-1}; NMR ($CDCl_3$) δ 1.61 (s, 3 H, Me), 4.01 and 4.90 (ABq, 2 H, *J* = 16 Hz, CH_2), 4.40 (s, 1 H, 4-H), 7.1–7.9 (m, 8 H, aromatic protons).

Anal. Calcd for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.91; H, 4.72; N, 13.17.

3-(*p*-Methoxybenzyl)-2-(*p*-methoxyphenyl)-5-methyloxazolidin-4-one (2f): bp 110 °C (10^{-3} torr) (bath temperature); IR ($CHCl_3$) 1685 cm^{-1}; NMR ($CDCl_3$) δ 1.54 (d, 3 H, *J* = 6 Hz, 5-Me), 3.46 and 4.85 (ABq, 2 H, *J* = 15 Hz, CH_2), 3.75 and 3.80 (two s, each 3 H, OMe), 4.43 (m, 1 H, 5-H), 5.62 (d, 1 H, *J* = 2 Hz, 2-H), 6.7–7.3 (m, 8 H, aromatic protons).

Anal. Calcd for $C_{19}H_{21}NO_4$: C, 69.70; H, 6.46; N, 4.27. Found: C, 69.29; H, 6.40; N, 4.20.

1-(*p*-Methoxybenzyl)-4-(*p*-methoxyphenyl)-3-hydroxy-3-methylazetidin-2-one (3f): mp 131–132 °C; IR ($CHCl_3$) 3360 and 1740 cm^{-1}; NMR ($CDCl_3$) δ 1.49 (s, 3 H, 3-Me), 3.75 and 4.80 (ABq, 2 H, *J* = 14 Hz, CH_2), 3.77 and 3.80 (two s, each 3 H, OMe), 4.22 (s, 1 H, 4-H), 6.7–7.4 (m, 8 H, aromatic protons).

Anal. Calcd for $C_{19}H_{21}NO_4$: C, 69.70; H, 6.46; N, 4.27. Found: C, 69.92; H, 6.43; N, 4.27.

3-(1-Adamantyl)-5-methyloxazolidin-4-one (2g): mp 82–83 °C; IR ($CHCl_3$) 1690 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (d, 3 H, *J* = 6 Hz, Me), 1.7 (br s, 6 H, adamantyl), 2.1 (br s, 9 H, adamantyl), 4.20 (q, 1 H, *J* = 6 Hz, 5-H), 5.05 (br s, 2 H, CH_2).

Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.45; H, 8.99; N, 5.95. Found: 71.35; H, 8.93; N, 5.92.

***N*-(-1-Adamantyl)-*N*-methoxymethyllactamide (7g)**: mp 73–74 °C; IR ($CHCl_3$) 3410 and 1640 cm^{-1}; NMR ($CDCl_3$) δ 1.30 (d, 3 H, *J* = 6 Hz, Me), 1.71 (br s, 6 H, adamantyl), 2.19 (br s, 9 H, adamantyl), 3.24 (s, 3 H, OMe), 3.85 (d, 1 H, *J* = 7 Hz, OH, D_2O exchangeable), 4.4 (m, 1 H, CHO), 4.45 and 4.68 (ABq, 2 H, *J* = 12 Hz, CH_2).

Anal. Calcd for $C_{15}H_{25}NO_3$: C, 67.38; H, 9.42; N, 5.23. Found: C, 67.33; H, 9.45; N, 5.25.

2,2-Dimethyl-3,5-diphenyloxazolidin-4-one (2k): mp 93–94 °C; IR ($CHCl_3$) 1700 cm^{-1}; NMR ($CDCl_3$) δ 1.59 (s, 6 H, Me), 5.48 (s, 1 H, 5-H), 7.1–7.9 (m, 10 H, aromatic protons).

Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.23. Found: C, 76.20; H, 6.40; N, 5.22.

4,4-Dimethyl-1,3-diphenyl-3-hydroxyazetidin-2-one (3k): mp 112–113 °C; IR ($CHCl_3$) 3320 and 1720 cm^{-1}; NMR ($CDCl_3$) δ 1.08 (s, 3 H, Me), 1.71 (s, 3 H, Me), 7.0–7.8 (m, 10 H, aromatic protons).

(24) Wigfield, D. C. *Tetrahedron* **1979**, *35*, 449.
(25) Campaigne, E.; Skowronski, G.; Rogers, R. B. *Synth. Commun.* **1973**, *3*, 325.
(26) Ratchford, W. P. *J. Org. Chem.* **1950**, *15*, 326.

Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.23. Found: C, 76.22; H, 6.41; N, 5.20.

Spectroscopic Detection of the Iminium Ions. NMR Spectra. A solution of the α-oxo amide (**1**) (5 mg) in 0.5 mL of CD_3OD containing D_2SO_4 (5%) was irradiated in an NMR tube with a 300-W high-pressure mercury lamp at -78 °C for 10-20 min. The NMR spectra were measurd at -50 °C immediately after the irradiation.

Visible Spectra. A solution of **1** (2-3 mg) in 3 mL of CH_3OH containing H_2SO_4 (5%) was irradiated in a cell for UV spectroscopy at -78 °C for 10-20 min. The visible spectra were recorded immediately after the irradiation.

Photolysis of Cyclohexyl Benzoylformate (12) in the Presence of Imines. The ester (200 mg) and an equimolar amount of the imine (6) were dissolved in dry benzene (10 mL). The solution was placed in a Pyrex tube and 1.5 g of molecular sieves (4 Å) was added. The tube was sealed, allowed to stand overnight, and then irradiated with a 1000-W high-pressure mercury lamp at 80 °C. After removal of the solvent, the product was isolated by flash chromatography on silica gel.

Acknowledgment. We thank Associate Professor O. Kikuchi for his helpful suggestions and discussions on the problems of diradicals and zwitterions. This research was supported by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan (No. 464160).

Registry No. 1b, 22381-21-1; **1c**, 64201-02-1; **1d**, 64201-00-9; **1e**, 84731-08-8; **1f**, 84731-09-9; **1g**, 84711-82-0; **1h**, 51804-83-2; **1i**, 40991-79-5; **1j**, 64201-19-0; **1k**, 84711-83-1; **2b**, 64201-17-8; **2d**, 64201-13-4; **2e**, 84711-90-0; **2f**, 84711-84-2; **2g**, 84711-91-1; **2h**, 64201-09-8; **2i**, 84711-85-3; **2j**, 64201-08-7; **2k**, 84711-86-4; **3d**, 64201-07-6; **3e**, 84711-87-5; **3f**, 84711-88-6; **3i**, 64201-01-0; **3j**, 64200-99-3; **3k**, 84711-89-7; **7b**, 84711-92-2; **7g**, 84711-93-3; **12**, 61598-01-4.

Alkoxides as Nucleophiles in (π-Allyl)palladium Chemistry. Synthetic and Mechanistic Studies

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Abstract: A new methodology for the use of alkoxides as nucleophiles in (π-allyl)palladium chemistry has been developed. In this process an allylic alcohol serves as the precursor to the π-allyl complex and a triethylsilyl (TES) ether as precursor to the alkoxide nucleophile. By using $Pd(PPh_3)_4$ in CCl_4, $PPh_3Cl^+CCl_3^-$ is generated transposing the ROH into an oxyphosphonium group, $R-O-P^+Ph_3$, and liberating Cl^-. The Cl deprotects the TES ether, providing the nucleophile in situ. Application of this reaction to the preparation of a variety of furans is discussed. This process was determined to proceed with overall predominant retention of configuration. Mechanistic studies suggest a small energy difference between attack by alkoxide on the allyl ligand of the intermediate complex and attack on the metal, followed by reductive elimination.

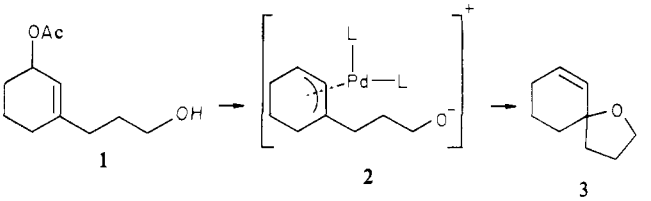
Introduction

Alkoxides have been of only limited utility as nucleophiles in (π-allyl)palladium chemistry. To date, only sodium salts of methanol, benzyl alcohol, and phenol have been successfully employed in transetherification reactions in synthetically useful yields.[1] As constituted, this process requires large amounts of palladium catalyst (2 equiv) and relatively high temperatures (60-85 °C).[1] In addition, the stereochemistry of this reaction has not been investigated further stifling its exploitation as a synthetic methodology.

Our efforts in the use of alkoxides in (π-allyl)palladium chemistry have resulted in the elucidation, including overall stereochemistry, of a process that occurs at modest temperatures, involves significantly smaller amounts of catalyst, and originates from a functionally simplified precursor. In addition, our studies of the mechanism and stereochemistry of this reaction suggest that alkoxides may exhibit a relatively small energy difference between the usual attack by nucleophiles on the allyl ligand and attack at the metal center followed by reductive elimination.

Results and Discussion

Preliminary Studies. Initial efforts centered on the preparation of the allylic acetate **1**, as a precursor to the required π-allyl complex **2**. Cyclization of **2** was expected to provide the spirofuran **3** in strict analogy with results obtained with carbon[2] and amine[3] nucleophiles. The synthesis of **1** was accomplished as outlined in Scheme I. The sequence was initiated by the reaction of the Normant Grignard[4] reagent derived from 3-chloropropanol with the vinylogous ester 3-ethoxy-2-cyclohexen-1-one. The resulting keto-alcohol **4** was converted to its triethylsilyl ether ((TES)Cl, NEt_3, THF, room temperature) and then reduced to the allylic alcohol **5** (DIBAL-H, $PhCH_3$, -40 °C). Acetylation (Ac_2O, NEt_3, DIMAP,[5] CH_2Cl_2, 0 °C) and desilation (NEt_3-HF, CH_3CN, 60 °C) provide **1** in 64% yield from the vinylogous ester. Treatment of **1** with any one of a variety of hydride bases (Li, Na, K) followed by 5-7 mol % of $Pd(DIPHOS)_2$ or $Pd(PPh_3)_4$ in refluxing THF resulted in destruction of catalyst and only poor yields of spirofuran **3**. Optimal yields (30%) were obtained by



1 2 3

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0002-7863/83/1505-1964$01.50/0