Photochemistry of *N*-Alkylpyrrolidinones in the Gas Phase and in Solution

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The gas-phase and solution-phase photochemistry of a series of *N*-alkylpyrrolidinones have been studied. In both cases the chemistry observed has been exclusively those processes initiated by type I cleavage. The type I gas-phase cleavage products, ethylene, carbon monoxide, 1,3,5-trimethyl-*s*-triazene, water, *N*-alkylazetidine, and *N*-alkylpyrrole, have been shown to be directly analogous to the products obtained from cyclopentanone. For example, labeling experiments have demonstrated that *N*-methylpyrrole from *N*-methylpyrrolidinone is the analogue of pentenal from cyclopentanone. In solution, pyrroles are the only products obtained. No evidence was found for the occurrence of any type II processes even in systems in which they would be favored on the basis of the cyclopentanone analogy. The photochemistry of pyrrolidinones closely parallels that of the cyclopentanones with respect to type I processes, but not with respect to type II processes.

As a part of our program to investigate the effects of a nitrogen atom on the photochemistry of carbonyl compounds, e.g., in amides, lactams, and imides, we investigated the photochemistry of a series of *N*-alkylpyrrolidinones.[2] The pyrrolidinone system is particularly attractive to study since the analogous ketone system, cyclopentanone, has been studied in such great detail[3-8] and can be used for comparison.

Results and Discussion

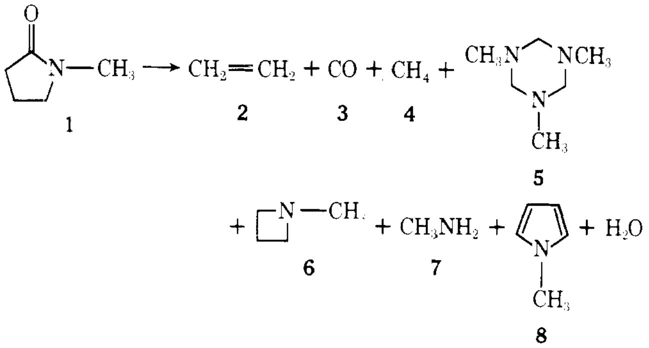
Gas-Phase Photolyses. Photolyses were carried out with and without mercury sensitization at 254 nm in the pressure range 50–100 torr. Products were continuously removed from the reaction cell and condensed in a liquid nitrogen cold finger. Subsequent product separation was achieved by bulb-to-bulb distillation and preparative GLC.

A number of products were obtained in the photolysis (Scheme I) including significant amounts of intractable polymeric material. Carbon monoxide, ethylene, and methane were identified by their infrared and mass spectra. The other products were identified by their NMR and IR spectra obtained on samples purified by preparative GLC.

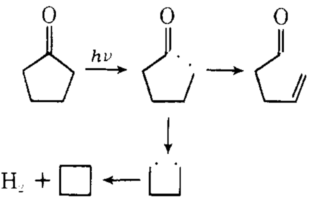
The mechanism for the formation of these materials is, for the most part, obvious on the basis of analogy with cyclopentanone (Scheme II). Initial α cleavage could occur at either the C–C(O) or C(O)–N bond to give biradicals **9** and/or **10** (Scheme III).

Biradicals **9** and **10** could then lose carbon monoxide to form biradical **11** which could either undergo closure to **6** or fragmentation to **2** and **12** which is known to undergo efficient trimerization to **5**.[9] Compound **12** is also the presumed precursor of methylamine via hydrolysis. There are two major mechanistic questions regarding product formation: (1) is the major source of **2** and **12** the biradical **11** or are they also generated by fragmentation of hot **6**; (2) what is the mechanism for the formation of *N*-methylpyrrole? Both of these questions were answered by deuterium-labeling experiments carried out on **1a** and **1b** (Table II).

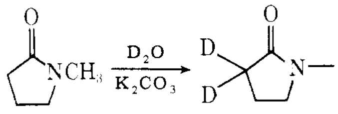
Scheme I



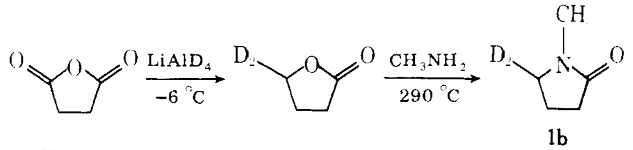
Scheme II



The labeled pyrrolidinone **1a** was conveniently prepared by exchange of **1** with D_2O in the presence of K_2CO_3.[10] The **1a** obtained contained 2% d_0 24% d, and 74% d_2. The reported preparation of **1b** via $LiAlD_4$ reduction of *N*-methyl succinimide[10] gave poor yields in our hands and required extensive GLC purification.

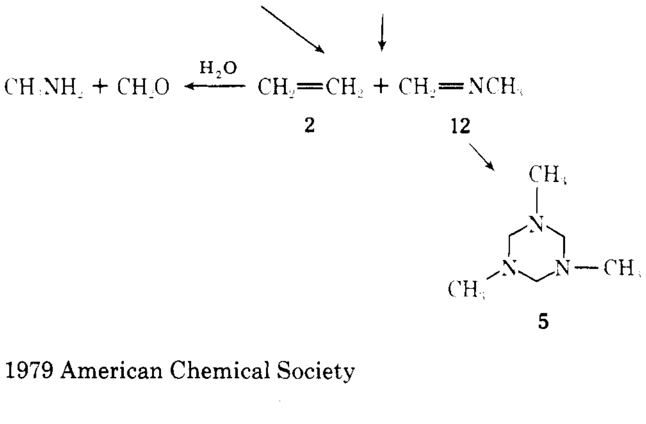


1 **1a**



1b

Scheme III



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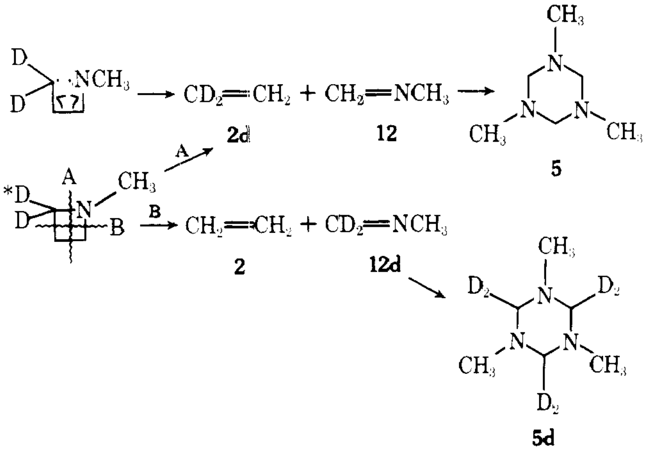
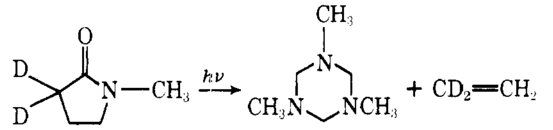
The method of choice involved careful LiAlD$_4$[11] reduction of succinic anhydride at −6 °C to the deuterated butyrolactone and treatment of the lactone with methylamine at 290 °C.[12] A low-voltage mass spectrum indicated that this material was 3% d_1 and 97% d_2 and the overall yield obtained was 30%.

The Precursor of Ethylene and *N*-Methylmethyleneimine. It appears a reasonable assumption that vibrational energy will be equally distributed over the equivalent bonds in "hot" **6**. In that case, two equivalent modes of cleavage of **6** exist which should occur with equal probability. This behavior has been observed in the low-pressure (<11 torr) photolysis of cyclopentanone whereas the direct cleavage of the tetramethylene biradical is the major process at higher pressures.[3]



Irradiation of **1a** was carried out at 50 torr and the IR spectrum of the ethylene obtained showed an out-of-plane bending deformation at 1384 cm^{-1}, consistent with that reported for **2d**,[13] whereas the corresponding absorption found in **2** at 1444 cm^{-1} was missing. The NMR spectrum of the triazine (**5**) was identical with that of the perhydro compound.



In a complementary experiment a sample of **1b** was photolyzed. The infrared spectrum of the ethylene formed showed weak absorptions at 1384 cm^{-1} from a small amount of deuterated ethylene, formed from photolysis of **1** partially deuterated at the 3 position, and a strong absorption at 1444 cm^{-1} from undeuterated ethylene. The NMR spectrum of the triazine showed a single resonance at δ 2.21 and no signal at δ 3.1 indicating that 1,3,5-trimethyl-*s*-triazine-*2,2,4,4,6,6,-d*$_6$ (**5d**) was formed. These results are only consistent with the generation of ethylene and *N*-methylmethyleneimine directly from biradical **12** as the major process as is also the case in the analogous cyclopentanone. No experiments were carried out at the low-pressure limit.

The Mechanism of Pyrrole Formation. The formation of *N*-methylpyrrole from **1**, formally a dehydration reaction, must involve intramolecular proton transfer, i.e., the carbonyl carbon in **1** must contain a proton in **8**. The most reasonable mechanism for the formation of **8** involves intramolecular hydrogen transfer in **9** to give imine aldehyde **13**, analogous to the formation of pentenal in the cyclopentanone photolysis.[5,6] Subsequent nucleophilic attack of the imine nitrogen on the carbonyl carbon and dehydration of **15** would afford **8**.

A critical labeling experiment involves deuteration at C5 in **1** since this mechanism requires C5 to C2 proton (or deuterium) transfer. The product pyrrole would then be doubly labeled at the α position. Photolysis of **1b** (97% d_2, 3% *d*) gave *N*-methylpyrrole with an α:β proton ratio of 0.17:2.0 (NMR), whereas the expected ratio is 0.04:2.00 based on the deuteration pattern in the starting material. The labeling results are consistent with the mechanism outlined in Scheme IV. The apparent loss of some of the label during the conversion of the **1b** to **8d** is explained by a reasonable isotope effect on the partition of biradical **9d** between decarbonylation (only secondary isotope effects involved) to **11** and intramolecular hydrogen abstraction (primary isotope effect involved) to **13d**.

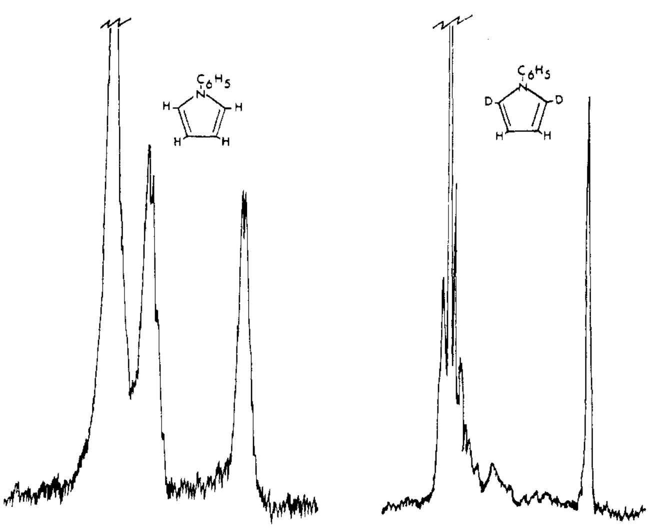
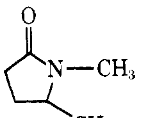
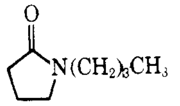


Figure 1. NMR spectra of *N*-phenylpyrrole and *N*-phenylpyrrole-*α,α-d*$_2$.

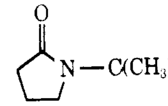
Similar labeling studies were carried out in solution using 1-phenylpyrrolidinone-*5,5-d*$_2$. The product obtained, 1-phenylpyrrole, was deuterated only in the α positions as shown by the complete absence of the δ 6.98 resonance present in the NMR of the perhydro compound indicating that the same mechanism is operative in solution.



1c



1d



1e

The vapor-phase photochemistry of three other pyrrolidinones, **1c–e**, was also studied. Photolysis of **1c** was carried out

Scheme IV

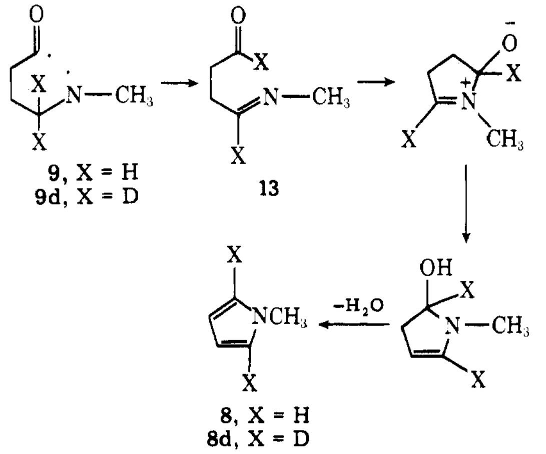


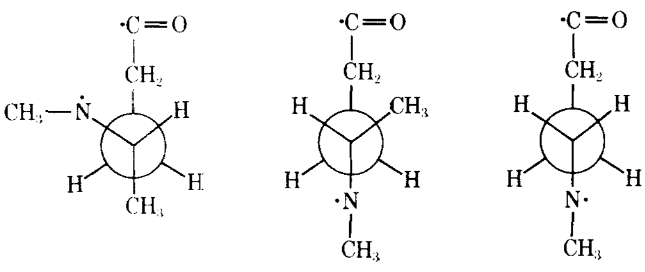
Table I. Product Distribution from Gas-Phase Photolysis

compd	CO[c]	C_2H_4[c]	azetedine	pyrrole	irradiation time, h
1[a,e]	0.25	0.20	0.05[d]	0.58[e]	21
1[a]	0.80	0.64	0.13[e]	0.19[e]	120
1[b]	0.68	0.54	0.14[d]	0.32[e]	22.5
1c[a,f]	0.50	0.33	0.17[d]	0.49[e]	116

[a] Direct irradiation. [b] Mercury sensitized. [c] Calculated from PV relationship and mass spectral analysis. [d] Assumed from stoichrometric relationship. [e] Measured by GLC. [e] Registry no. 872-50-4. [f] Registry no. 5075-92-3.

with and without mercury sensitization and in both cases carbon monoxide, ethylene, methylamine, 1,2-dimethylmethyleneimine, and 1,2-dimethylazetidine were detected. No evidence was found for the formation of any 1,2-dimethylpyrrole. This result was surprising in that pyrroles were the ubiquitous products of all the 1-alkyl pyrrolidinone photoreactions in the vapor phase and in solution (vide infra). It is possible that substitution caused a significant change in the relative efficiencies of bond cleavages such that 2,3 bond cleavage was occurring at the expense of 1,2 cleavage. However, it seemed unlikely that 5 substitution would dramatically affect the rate of 1,2-bond cleavage so that potential biradical **10** would form at the expense of **9** (Scheme III).

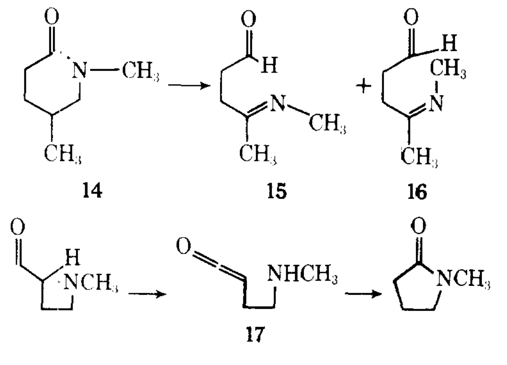
A second possibility was that the biradical from **1c** (**14**) preferred to reclose to **1c** or fragment rather than undergo intramolecular hydrogen abstraction to iminealdehyde. This idea has some validity in that, of the two conformations which can lead to imine aldehyde (A and B) conformer A is positioned to reclose to pyrrolidinone. Such is not the case with the 1-substituted pyrrolidinone where the most stable conformer of the biradical, C, favors hydrogen abstraction.



A B C

Steric considerations make it obvious that only the *trans* imine **15** can effectively close to pyrrole, i.e., in the corresponding cis isomer, **16**, the *N*-methyl group would hinder the attack of the free electron pair on nitrogen at the carbonyl carbon. It is quite possible that photolysis of **1c** could lead to an imine isomer distribution richer in the cis imine **16** than the trans isomer **15**. This prediction follows from conformational analysis based on results found in 2-methylcyclohexanone[15] and would lead to a decrease in pyrrole formation.

An important consideration is the statistical factor due to the number of hydrogens available for abstraction in **9** vis-à-vis **14**. In the corresponding ketone cases (solution) this



14 15 16

17

Table II. Products from Photolysis of Labeled Pyrrolidinone

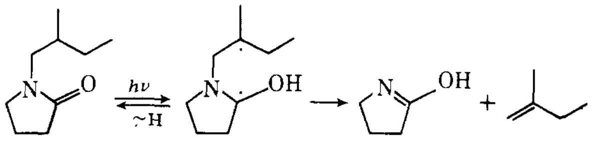
pyrrolidinone	products
1	**2** + **5** + **8**
1a	**2d** + **5**
1b	**2** + **5d** + **8d**

results in a marked decrease in the eneal–ketene ratios. In our case we expect that the corresponding ketene **17** would not be observed since it should efficiently reclose to starting material.

The photolysis of **1d** and **1e** was investigated to see if a type II cleavage of the *N*-alkyl group would be observed. Mercury sensitized irradiation of **1d** was conducted and evidence for the formation of ethylene, carbon monoxide, 1-*n*-butylazetidine, and 1-*n*-butylpyrrole (IR, NMR) obtained. IR gas analysis showed no evidence for the formation of 1- or 2-butene and GLC analysis indicated the absence of 2-pyrrolidinone. Direct irradiation of *N*-*tert*-butyl-2-pyrrolidinone gave ethylene, carbon monoxide, *N*-*tert*-butyl pyrrole, 1-*tert*-butylmethyleneimine, and 1-*tert*-butylazetedine (Table I). Again no evidence for the formation of isobutylene (IR) and pyrrolidinone (GLC) was obtained under experimental conditions to which these products are stable. It is clear that the type II process is at best a minor contributor to the photodecomposition of pyrrolidinone in the gas phase.

Solution Studies. A similar series of experiments were carried out in solution with a variety of N-substituted pyrrolindinones (**1e–l**) and in all cases the corresponding pyrrole was the *single* product formed.[17,18] This is consistent with results found in cyclopentanones to the extent that no decarbonylation is observed in solution but is inconsistent with results in 2-substituted cyclopentanones where the type II process is significant in favorable cases.[19] In no case where the type II process was possible (**1e–j**) did we observe the formation of any pyrrolidinone. Control experiments indicated that pyrrolidinone was sufficiently stable to the reaction conditions to accumulate during the course of the reaction. GLC detection limits suggest that the maximum amount of pyrrolidinone which could have formed and gone undetected would be less than 2% of the pyrrole formed.

The absence of type II products could be explained in two ways. Either the type II abstraction to give biradical **18** does not occur or once **18** is formed it undergoes a reaction or reactions other than secondary cleavage to alkene and pyrrolidinone. One reasonable possibility is that **18** back transfers a hydrogen to regenerate starting material in a quantum wasting step. That this might be an efficient process in this system is suggested by electronic overlap considerations.



lm 18

Table III. Quantum Yields for Pyrrole Formation

			Φ_{rel}		Φ	
registry no.	compd	R	2-propanol	*tert*-butyl alcohol	2-propanol	*tert*-butyl alcohol
	1	CH_3	0.16	0.44	0.011	0.03
2687-91-4	**1f**	CH_2CH_3	0.03	0.03	0.002	0.002
3470-99-3	**1g**	$CH_2CH_2CH_3$	0.18		0.012	
2687-92-5	**1h**	$CH_2CH(CH_3)_2$	0.25	0.28	0.017	0.019
20687-53-0	**1e**	$C(CH_3)_3$	1.0	0.73	0.068	0.050
58244-30-7	**1i**	$CH(CH_3)CH_2CH_3$	0.46	0.29	0.031	0.019
10135-23-6	**1j**	$CH_2CH_2C_6H_5$		0.03		0.002
4641-57-0	**1k**	C_6H_5	0.68	1.17	0.046	0.080
5291-77-0	**1l**	$CH_2C_6H_5$	~0	0.01	~0.0	~0.001

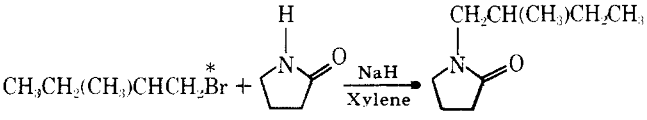
Table IV. Quantum Yields for Product Formation[18,23]

$C_6H_5\overline{NCO(CH_2)_n}$	registry no.	Φ
19a, $n = 2$	5099-95-6	0.024–0.044^a
b, $n = 5$	105-60-2	0.071^b
c, $n = 6$	673-66-5	0.11^b
d, $n = 11$	947-04-6	0.082^b

^{a} Cleavage to ketene and imine or alkene and isocyanate; Φ varies with substitution. Methanol solvent. ^{b} Rearrangement to the corresponding 1-azabenzocycloalkeneone. Ethanol solvent, irradiated at 254 nm.

Stabilization of the radical center on carbon by the free-electron pair on the adjacent nitrogen requires that these orbitals be coplanar. This forces the p orbital on carbon to be orthogonal to the C–N σ orbital and precludes an efficient secondary cleavage step. This is observed in the related N-substituted phthalimide[20] and succinimide[21] systems where the corresponding biradical closes to the azacyclobutanol rather than undergoing type II cleavage.

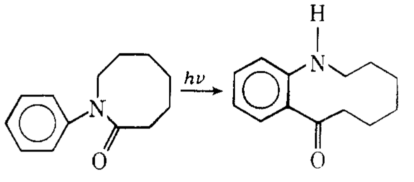
We investigated the back-transfer process by studying the optically active lactam **1m** $[\alpha]^{20}_{313}$ −6.3 ± 0.2 (*c* 0.0285, absolute ethanol) prepared by alkylation of pyrrolidinone with optically active 2-methyl-1-bromobutane.[22] This lactam was irradiated under the usual conditions to >50% conversion and starting material reisolated. The unreacted **1m** showed $[\alpha]^{20}_{313}$ −6.2 ± 0.2 (*c* 0.0285, absolute ethanol), unchanged from the initial starting material. Since the **1m** $\rightleftarrows$ **18** equilibrium is expected to result in racemization of **1m**, it is clear that this is not an important process.



1m

The quantum yields for product (pyrrole) formation could also provide information on the relative efficiency of the type II abstraction process. If the initially formed biradical is siphoned off to other (nonisolated) products, the quantum yield for pyrrole formation might be expected to decrease as the efficiency of type II abstraction increased. However, there are a number of dark steps (Scheme IV) which must take place after the initial photochemical act (H abstraction) to produce pyrrole, and small differences in quantum yields could be the result of steric or electronic substituent effects on these steps which would be very difficult to assess.

The efficiency of γ-hydrogen abstraction should follow the order **1** = 0 < **1f** < **1g** < **1h** and correspondingly, we would expect the efficiency of pyrrole formation to follow the order **1** > **1f** > **1g** > **1h**. It is clear that the quantum yields (Table III) do not follow the expected order. The values obtained are in the range expected from analogy with other lactam photorearrangements which are initiated via α cleavage,[18,23] e.g., **19b** → **20** (Table IV).



19b **20**

Discussion

In previous studies by Nicholls and Leermakers[24] and us[25] it has been established that the type II process is, at best, a minor contributor to the photochemistry of alkylamides. The present work shows that the major process occurring on irradiation of pyrrolidinone is also the type I cleavage. With regard to type I processes the analogy between pyrrolidinone and cyclopentanone is remarkable in a qualitative sense. The vapor-phase products from pyrrolidinone are closely matched by those of cyclopentanone after it is recognized that pyrrole formation corresponds to pentenal formation from cyclopentanone. This study also firmly established that C(O)–N bond cleavage is an important process in solution and in the gas phase since pyrrole may only result from this cleavage. We cannot rule out C–C(O) cleavage as a competing route since the formation of other gas-phase products can be rationalized on this basis and the material balance in the solution work (34% yield of *N*-phenylpyrrole)[18] is not good.

Our evidence indicates that type II processes are unimportant in pyrrolidinones. By analogy the corresponding ketone system affords a 20% yield of type II product when the γ hydrogen is tertiary, e.g., 2-isobutylcyclopentanone, and it is estimated that the triplet rate constant is 1–2 × 10^9 s^{-1}.[19]

Clearly the amide carbonyl is less reactive to hydrogen abstraction than the ketone carbonyl[19,26] and this has been ascribed to the existence of charge transfer excited states by Leermakers.[24] It is noteworthy that acids and esters undergo the type II cleavage with reasonable efficiency.[24,27]

We suggest that the lack of type II reactivity in amides and lactams is best explained by considering the effect of the atoms or groups α to the carbonyl. Ditchfield, Del Bene, and Pople[28] have calculated that the n–π^* states of amides should be more electron rich on the carbonyl oxygen than the corresponding states in ketones and acids. Although their spectral characteristics are similar, the excited state electron distributions in acids and amides are different due to variation in the π donation and σ withdrawing properties of oxygen vis-à-vis nitrogen. Oxygen is a poor π electron donor and a good σ electron withdrawer whereas π donation from nitrogen is quite efficient and σ electron withdrawal relatively inefficient. Since the effect of π donation is to make the carbonyl oxygen electron rich and σ withdrawal makes it electron poor, in its excited state the amide oxygen is less electrophilic then the carbonyl oxygen in acids and esters. Since it is well known that type II processes occur most efficiently through electrophilic

$n \rightarrow \pi^*$ states[26] the amides should show the observed lack of reactivity. N substituents which decrease the π donating efficiency of nitrogen should confer type II reactivity. This has been observed through the addition of a second carbonyl group on the nitrogen in the imide system. The phthalimides[20] undergo type II abstraction and our studies on alkyl imides have shown that they undergo type II cleavages from the singlet and triplet states but with triplet rate constants still several orders of magnitude lower than those found for the corresponding ketones.[29]

Experimental Section

Microanalyses were performed by Dr. Franz Kasler of the University of Maryland, Department of Chemistry. IR spectra were obtained on a Beckman IR-8 grating spectrophotometer, as potassium bromide pellets or neat between salt plates. NMR spectra were obtained on a Varian A-60 D or a Hitachi Perkin-Elmer R-20A NMR spectrophotometer in carbon tetrachloride solutions with tetramethylsilane as internal standard unless otherwise noted. All mass spectra were obtained on a Bell and Howell 492 mass spectrometer. Preparative GLC work was done on a Varian Aerograph A-90 using a thermal conductivity detector and the analytical GLC work on a Varian Aerograph series 1200 or a Gow-Mac Series 730 with flame ionization detectors. Rotations were measured on a Cary 60 ORD instrument.

Vapor-Phase Photolyses. The general procedure is described in detail below for 1-methylpyrrolidinone. Vapor-phase studies on other materials were carried out in a similar manner. Products were generally identified by comparison of their IR and NMR spectra with those of authentic samples when available. Results are presented in the Discussion section.

After the system[30,31] had been checked for leaks, a weighed sample was submitted to four freeze-pump-thaw cycles and the sample holder was rotated 180° to empty the sample into the reactor. The temperature and pressure were adjusted to bring the sample to reflux and the temperature of the walls of the reactor adjusted so that none of the reactant condensed on the walls. Because the generation of carbon monoxide during photolysis causes an increase in pressure, the pressure of the system was readjusted periodically rather than raising the temperature to maintain a constant rate of reflux. During photolysis, the temperature was maintained constant by means of a Fenwal thermostat which holds the temperature within ±3 °C of the setting. Gas samples were taken during the pressure adjustment for analysis by IR. Typically for a mercury-free system an exposure of 120 h was needed to photolyze about 6 mmol of pyrrolidinone reactant whereas in a mercury-sensitized reaction about 16 mmol photolyzed in 12 h. During the photolysis the liquid gradually changed color from water white to yellow to brown.

Photolysis of 1-Methyl-2-pyrrolidinone. With and without mercury sensitization, 1-methyl-2-pyrrolidinone has been studied over the pressure range 50–100 mm Hg (115–135 °C). The vapor was irradiated with 2537-Å light from a bank of germicidal lamps and the products collected in a liquid nitrogen cold trap. Gaseous products were transferred under vacuum to a 10-cm infrared gas cell connected to the vacuum line.

With liquid nitrogen in the cold trap, the only volatile product was carbon monoxide in the mercury free system; measurements made over several reactions gave an average rate of pressure drop of 0.23 mm/h which is linear up to 100 h of irradiation. Carbon monoxide was characterized by IR. In mercury-sensitized reactions, particularly those of long duration, methane was also present based on IR evidence.

Carbon monoxide was pumped out of the system and dry ice was substituted for the liquid nitrogen in the cold trap. Ethylene was the only gas present and was characterized by its IR spectrum. Mass spectral analysis of the unseparated mixture of carbon monoxide and ethylene indicated the ratio of the two compounds was 5 to 4 in a mercury-free system.

During photolysis a waxy deposit accumulated on the cold finger. This compound has a melting point of 47–49 °C and its IR and NMR spectra were identical with those of an authentic sample of 1,3,5-trimethylhexahydro-*s*-triazine.[9]

Ethylene was pumped out of the system, an ice water mixture substituted for dry ice, and methylamine distilled to a liquid nitrogen cooled bulb. The distilled material was identified as methylamine by IR and NMR spectroscopy.

The remainder of the material in the cold trap was distilled and IR analysis indicated that it was a mixture of methylamine, 1-methylazetidine, water, and 1-methylpyrrole. The mixture was separated by preparative GLC on a pair of sequential columns: 15% Carbowax 400 on 100/120 Chromosorb W coated with 4% KOH, 7 ft × 1/4 in., 15% ethanolamine on 100/120 Chromosorb W coated with 4% KOH, 2 ft × 1/4 in. Pyrrole (retention time = 62 min) was identified by its IR and NMR spectra. 1-Methylazetidine (retention time = 4.5 min) showed: H^1 NMR ($CDCl_3$) δ 1.9 (t, J = 7 Hz, 2 H), 3.08 (t, J = 7 Hz, 4 H), 2.15 (s, 3 H), corresponding to those reported by Higgins;[32] IR (neat) 2870, 2820, 1238, 1200, 1150 cm^{-1}. This material rapidly solidifies to a reddish brown solid on standing.

A number of quantitative experiments were carried out using dodecane as an internal standard for nongaseous products. The amount of ethylene and carbon monoxide produced was measured from the pressure increase during the irradiation, the volume of the reactor, and the mass spectral ethylene–carbon monoxide ratio of 4:5. The contents of the reactor were distilled to the cold trap and analyzed by GLC. In a typical reaction a 4.52-g sample gave 4.25 g (94%) of recovered material. No attempt was made to determine the amount of methylamine or triazene produced as these quantities are implicity given by the quantity of ethylene produced. Methylamine presumably arises from hydrolysis of *N*-methylmethyleneimine or triazene. The quantity of 1-methylazetidine was implied from the deficiency of ethylene to carbon monoxide and the reaction mechanism. A measurement of 1-methylazetidine production (Table I) showed this correlation to be valid. The quantity of pyrrole measured is a lower limit as indicated by the fact that 7.0×10^{-3} mol of water but only 1.5×10^{-3} mol of pyrrole were produced in a 120-h irradiation.

Since water is a by-product of pyrrole production and it is partially consumed in methylamine production, the quantity of pyrrole measured must be low by at least a factor of 5 in this experiment. Apparently pyrrole is undergoing thermal and/or photodegradation. This is also indicated by the greater pyrrole–ethylene ratio found at shorter irradiation time.

1-Methylpyrrolidinone-*5,5-d*$_2$. (a) γ-Butyrolactone-*5,5-d*$_2$. In a nitrogen atmosphere, 200 mL of THF was distilled from $LiAlH_4$ into a 1-L round-bottom flask and 2.20 g (0.0520 mol) of $LiAlD_4$ was added to it. The stirred mixture was refluxed for 30 min and then cooled to −6 °C with a dry ice–acetone bath. A solution of succinic anhydride (10.0 g, 0.100 mol) in 150 mL of THF was added to the cold $LiAlD_4$ solution as rapidly as possible. The stirred mixture was allowed to warm to 10 °C over a period of 1 h and 2 mL of water, 2 mL of 15% NaOH, and 6 mL of water, in that order, were added to the stirred mixture. The solution was allowed to warm up to room temperature and filtered. The filtrate mixture was evaporated in vacuum to yield an oily residue. The filter cake was dissolved in 80 mL of 6 N H_2SO_4, salted out with solid $MgSO_4$, and extracted with four 30-mL portions of ethyl ether. The extract was combined with the previous filtrate residue, dried over $MgSO_4$, filtered, and evaporated in vacuum. Distillation of the residue gave 4.47 g (51%) of product: bp 44 °C (0.6 mm); IR (neat) 2260, 2200, 2140, and 1750 cm^{-1}. The triplet at δ 4.4 in the ^1H NMR of butyrolactone was absent in the spectrum of this material.

(b) Conversion of Deuterated Lactone to 1-Methylpyrrolidinone. A mixture of 20 mL of anhydrous methylamine and 3.38 g (0.038 mol) of deuterated lactone was placed in a high-pressure reactor. The reactor was heated at 290 °C for 3 h and cooled to 0 °C; the reaction mixture was removed using ether as a transfer agent. Solvent and methylamine were removed by evaporation and the residue distilled to afford 2.25 g (58%) of product: bp 53–54 °C (0.6 mm); IR (neat) 2100, 2200, and 1680 cm^{-1}. The ^1H NMR was similar to that of unlabeled material except that the triplet at δ 3.38 was absent. Mass spectral analysis indicated the material was 3% d_1 and 97% d_2. All other pyrrolidinones were prepared in a similar manner unless otherwise noted.

Irradiation of this material in the normal manner gave 1,3,5-trimethyl-2,4,6-triazine-*2,2,4,4,6,6-d*$_6$ (**5d**), based on the absence of the normal CH_2 resonance at δ 3.1, and 1-methylpyrrole-*2,5-d*$_2$ based on an α:β proton ratio of 0.17:2.0 in the ^1H NMR.

Solution Studies. 1-Phenylpyrrolidinone-*5,5-d*$_2$. This material, prepared from labeled butyrolactone, was irradiated in 2-propanol solvent as previously described.[18] The NMR spectrum of the product showed the absence of α proton absorption at δ 6.98. Only *N*-phenyl and β-proton resonances at δ 7.27 (5 H) and 6.26 (2 H), respectively, were present.

1-(2-Methylbutyl)-2-pyrrolidinone. A 3.8-g (0.08 mol) sample of 50% sodium hydride was washed with xylene to remove the paraffin oil and then 6.8 g (0.08 mol) of 2-pyrrolidinone in 20 mL of xylene was added slowly with stirring under nitrogen. After the foaming subsided, the mixture was heated for 1 h at 110 °C, optically active 1-bromo-2-methylbutane (9.4 g, 0.06 mol) was added to the salt, and the mixture was heated at reflux overnight. The reaction mixture was washed with 10 mL of water and solvent removed by distillation. The residue was distilled to give 4.1 g (44%) of product, bp 115 °C (9 mm). This material was purified by preparative GLC on a 9 ft × $\frac{1}{4}$ in. column packed with 20% SE-30 on 60/80 Chromosorb W before use. This material showed a rotation of $[\alpha]^{20}{}_{313}$ −6.3 ± 0.2 (*c* 0.0285, absolute ethanol). A solution of 2 g of this pyrrolidinone in 300 mL of 2-propanol was irradiated until 50% of the starting material was consumed (GLC). Solvent was removed by distillation and unreacted starting material purified by preparative GLC. This material showed a rotation $[\alpha]^{20}{}_{313}$ −6.3 (0.0286, absolute ethanol).

Quantum Yields. Samples consisted of the pyrrolidinone (2 M) in 2-propanol or 2-methyl-2-propanol containing either nonane or decane internal standards. All pyrrolidinones were purified by preparative GLC. Samples were placed in 1.0 × 16 cm quartz tubes, subjected to three freeze–pump–thaw cycles to remove dissolved gases, and sealed at 10^{-6} torr. Samples were irradiated, in triplicate, in a merry-go-round apparatus surrounded by a bank of ten GE 15-T8 germicidal lamps whose principal emission is at 254 nm. The formation of pentenal from cyclopentanone was used as actinometer.[5] Since the pyrroles produced in these reactions have molar absorptivities approximately 100 times larger than those of the pyrrolidinones at the irradiating wavelength (254 nm), conversions were held to below 1% to prevent product competition for the light. Samples were analyzed by GLC on either of the following columns: 20% SE-30 on 100/120 Chromosorb WHP, 6 ft × $\frac{1}{4}$ in.; 3% OV-17 on 100/120 Chromosorb WHP, 6 ft × $\frac{1}{8}$ in. Quantum yield data are presented in Table III.

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Registry No.—**1a**, 932-07-0; **1b**, 68036-46-4; **1d**, 3470-98-2; methylamine, 74-89-5; 2-pyrrolidinone, 616-45-5; 1-bromo-2-methylbutane, 10422-35-2; 1-(2-methylbutyl)-2-pyrrolidinone, 58244-31-8; 1-methylazetidine, 4923-79-9; γ-butyrolactone-*5,5-d*$_2$, 68036-47-5; succinic anhydride, 108-30-5.

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Selective Codimerization of Acetylenes and Allyl Halides Catalyzed by Palladium Complexes

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The reaction of various acetylenes and allyl halides with palladium complexes selectively gives substituted 1,4-diene codimers. The $PdX_2(PhCN)_2$ complex is the most active catalyst. In contrast to substituted acetylenes, the reaction of acetylene itself and allyl halides gives a 1-halogeno-1,3,6-heptatriene cotrimer besides codimers. The catalytic reaction proceeds via Pd–halogen bond recycle; initially acetylene inserts into a Pd–halogen bond and subsequently allyl halide inserts into a Pd–vinyl bond, followed by the β-halogen elimination to give a codimer. The successive insertions of acetylene and allyl halide into the Pd–vinyl bond give a cotrimer. This codimerization provides a very convenient synthetic method for halogeno-substituted mono- and/or diolefins.

Homooligomerization of acetylenes or olefins using transition metal catalysts has been extensively studied.[1] However, only a few examples are known of cooligomerization of acetylenes and monoolefins[2–6] probably because of the difficulty caused by the large difference in coordination ability between acetylenes and olefins to metal center; acetylenes are much more reactive to metals than olefins are, which results in exclusive polymerization of the acetylenes. Concerning palladium catalysts, only two examples have been reported. One is a linear cotrimerization of diphenylacetylene and olefins,[5] and the other is a cyclic cotrimerization of dimethoxycarbonylacetylenes and norbornene.[6] The diphenylacetylene and dimethoxycarbonylacetylene used above have a relatively lower reactivity to palladium when compared with common acetylenic compounds. Therefore, in order to accomplish the cooligomerization of acetylenes and olefins, it is very important to select suitable acetylenic or olefinic compounds with similar orders of coordination ability to a metal, or to devise reaction conditions in which extensive acetylene polymerization is prevented. We have found that the selective codi-