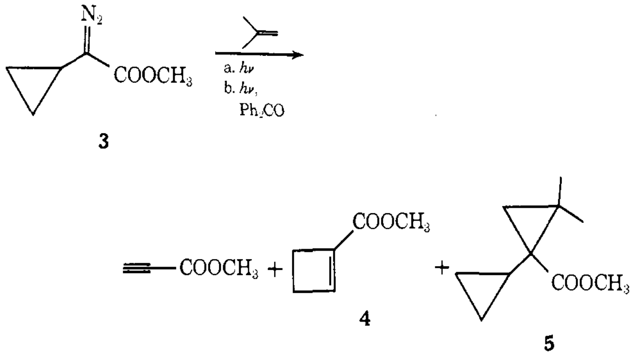
cordingly, we synthesized diazo compound **3** from the appropriate pyruvate and studied its decomposition. In this case the anticipated products of intramolecular reaction were 1-carbomethoxycyclobutene (**4**) and methyl propiolate, the former produce by ring expansion and the latter by fragmentation.

The direct irradiation of **3** in benzene gave 67% **4** and 18% methyl propiolate. A benzophenone sensitized decomposition under the same conditions reduced the amounts of products to 14% **4** and 16% propiolate. Cyclobutene **4**, however, is rapidly polymerized on sensitized irradiation in benzene (but not by unsensitized), and the yield of **4** is a minimum value. In isobutylene solvent direct irradiation gave 3% propiolate, 20% **4**, and 8.5% of an adduct **5**. When the decomposition in isobutylene was sensitized with benzophenone, the yield of **5** increased to 33%, propiolate was unchanged, and the yield of **4** fell to 11% (again this is a minimum value). Thus, intermolecular reaction can be increased, but the intramolecular reactions cannot be as efficiently suppressed as in the case of **1**.



a,	3%	20%	8.5%
b,	3%	11%	33%

In summary, we have shown that intramolecular reactions of alkylcarbomethoxycarbenes can be reduced by generation of the triplet state and that this reduction is less efficient when the model free radical reactions are efficient ones.

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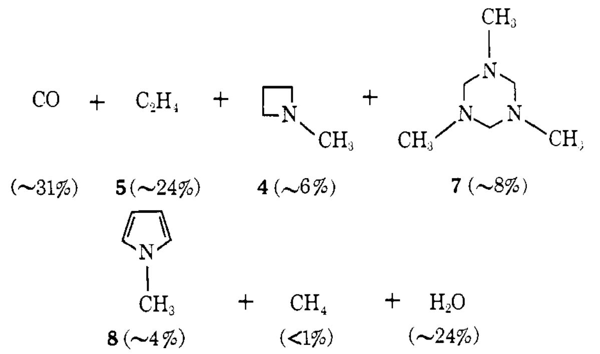
Photolysis of *N*-Methyl-2-pyrrolidone

Sir:

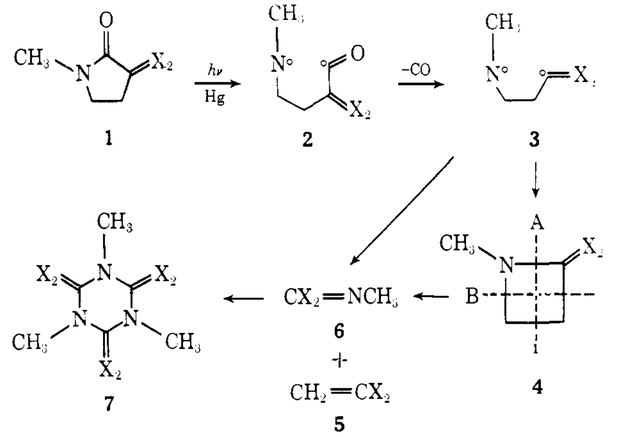
The photochemistry of carbonyl compounds, especially ketones and aldehydes, has been the subject of intensive investigation for some time.[1,2] One of the areas that has received relatively little attention is the photochemistry of lactams and, while there have been studies carried out on the solution photochemistry of several *N*-phenyl derivatives,[3,4] the vapor-phase photochemistry of simple lactams has been neglected.

We initiated our work on lactams by studying the vapor-phase photodecomposition of *N*-methylpyrrolidone (**1**). This molecule was a particularly attractive candidate since the photochemistry of cyclopentanone, which we intended to use as a model system, had been studied in great detail.[5,6]

Irradiation[7] of **1** (Hg sensitized) led, in addition to extensive polymer formation, to the products listed below.



The mechanism of formation of most of these products is clearly analogous to the cyclopentanone case involving either a stepwise[8] (*via* **2**) or concerted[9] loss of carbon monoxide to give diradical **3**.[10] This species



1–7, X = H; **1a–7a**, X = D

could either cleave to ethylene and *N*-methylimine, isolated and characterized as its known trimer 1,3,5-trimethylhexahydro-*s*-triazene (**7**), or close to afford the azetedine **4**. Alternatively, **5** and **6** might arise from a thermal reaction of "hot" **4**.[5] A decision could be arrived at on the basis of the results from photolysis of **1a**.[11] If cleavage of **3a** were the major process occurring, **5a** and **6** (isolated as **7**) should be obtained. However, if **4a** was an important intermediate a mixture

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(1) J. N. Pitts, Jr., and J. K. S. Wan in "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience, New York, N. Y., 1966, pp 823–915.

(2) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 377.

(3) M. Fischer, *Chem. Ber.*, 102, 342 (1969).

(4) M. Fischer, *ibid.*, 101, 2678 (1968); *Tetrahedron Lett.*, 2281, 4295 (1969).

(5) A. T. Blades, *Can. J. Chem.*, **48**, 2269 (1970).

(6) C. Y. Mok, *J. Phys. Chem.*, 74, 1432 (1970).

(7) Preparative reactions were carried out in heated quartz tubes at 30–100 mm pressure with 2537-Å light and mercury sensitization. Volatile products were collected in cold traps. The reaction also took place at 2537 Å without sensitization but with markedly decreased efficiency. Runs on **8a** were carried out in a mercury-free system.

(8) R. L. Alumbaugh, O. Pritchard, and B. Rickborn, *J. Phys. Chem.*, **69**, 3225 (1965).

(9) R. Srinivasan, *Advan. Photochem.*, 1, 83 (1963).

(10) For convenience only one of a pair of possible diradicals, **2**, is shown. Cleavage of the carbon–carbon bond to give $\cdot CON(CH_3)CH_2CH_2CH_2\cdot$ is also possible and would afford **3** on decarbonylation.

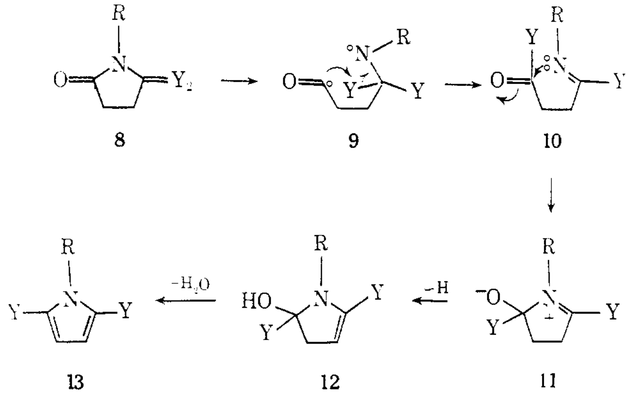
(11) A. M. Duffield, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, **86**, 5536 (1964).

of **5**, **5a**, **6**, and **6a** isolated as **7** and **7a** was expected; *i.e.*, **4a** has two equivalent cleavage pathways: A, which would lead to **5a** and **6**, and B, which would lead to **5** and **6a**.

An infrared spectrum of the ethylene obtained on irradiation of **1a** showed absorptions at 3017, 2230, 1585, 1384, 943, and 751 cm^{-1}, identical with those reported[12] for **5a**. In addition, the nmr spectrum of the *s*-triazene obtained was identical with that of **7** indicating that there was no deuterium incorporation. Clearly, under these experimental conditions **4** is not an important intermediate to the formation of **5** and **6**.

Of particular interest is *N*-methylpyrrole (**13**) formation which formally corresponds to dehydration of **1**. *N*-Phenylpyrrole (**13b**) has been reported[3] as the sole product isolated from irradiation of **8b** in solution but its mode of formation was not commented on. The close analogy to the photochemistry of cyclopentanone, which affords 4-pentenal as a major product, led us to speculate on the absence and possible fate of the nitrogen analog of this material, **10**, in the present case. In fact, the route **10** → **13** appeared to be an attractive one for the formation of pyrrole.

Photolysis of material labeled in the 5 position provided a critical test for the intermediacy of **10** since this mechanistic scheme requires deuterium transfer (in **8a** or **8c**) from C$_5$ to C$_2$. Subsequent dark steps would result in α,α'-labeled pyrroles **13a** or **13c**.



8–13, R = CH$_3$; Y = H
8a–13a, R = CH$_3$; Y = D
8b–13b, R = C$_6$H$_5$; Y = H
8c–13c, R = C$_6$H$_5$; Y = D

The nmr spectrum of the volatile condensate obtained on direct irradiation of **8a**[13] showed the expected resonances at τ 6.59 (NCH$_3$) and 4.05 (β H) but the resonance at τ 3.65 present in the spectrum of **13** (α H) was absent. Similarly, the spectrum of the *N*-phenylpyrrole isolated from irradiation of **8c** in 2-propanol showed resonances at τ 2.72 (C$_6$H$_5$) and 3.85 (β H). These data are only consistent with the formation of **13a** and **13c** from **8a** and **8c**, respectively, and clearly demonstrate the intermediacy of **10** in the formation of **13**.

The vapor-phase photochemistry of *N*-methyl-2-pyrrolidone, at least with respect to product formation, is strikingly similar to that of cyclopentanone. Whether this close analogy holds for the quantitative aspects of this reaction is a question which must await the results of further studies.

Acknowledgment. We are indebted to the Center of Materials Research of the University of Maryland for partial support of this work.

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(12) W. J. Lehman, *J. Mol. Spectrosc.*, 7, 3 (1961).

(13) Compounds **8a** and **8c** were prepared by heating the corresponding amine and butyrolactone-*4,4-d*$_2$ (prepared by LiAlD$_4$ reduction of succinic anhydride[14]) in sealed tubes.

(14) J. J. Bloomfield and S. L. Lee, *J. Org. Chem.*, **32**, 3919 (1967).

(15) National Science Foundation Science Faculty Fellow, 1970–1972.

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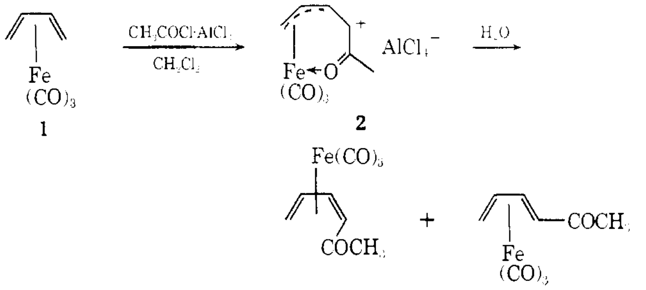
Reactivity of Tricarbonyl(diene)iron Compounds toward Electrophiles and Charge Distribution in Tricarbonyl(π-allyl)iron Cations

Sir:

Tricarbonyl(diene)iron compounds undergo facile Friedel–Crafts acylation to give *cis*- and *trans*-tricarbonyl(dienone)iron compounds.[1-3] Acetylation of tricarbonyl(butadiene)iron (**1**) was shown to proceed *via* the isolable ionic intermediate **2**.[2a] Lack of substitution at internal diene carbons is attributable to the relative instability of the requisite tricarbonyl(π-homoallyl)iron cation intermediate.[2,4] Rate-determining electrophilic attack of the methyloxocarbonium tetrachloroaluminate ion pair[5] should proceed *via* a transition state which resembles a tricarbonyl(π-allyl)iron cation.[6] Substituent effects on electrophilic reactivity of the diene complexes[7] would provide a basis for determining charge distribution in tricarbonyl(π-allyl)iron cations and for evaluating the general synthetic utility of the acylation reaction.



We have assessed the relative reactivity in acylation of several substituted diene complexes by allowing each to

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(1) G. G. Ecke, U. S. Patent 3,149,135 (1964). Acylation at C$_2$ reported in this patent has been shown to be in error.[2]

(2) (a) E. O. Greaves, C. R. Knox, and P. L. Pauson, *Chem. Commun.*, 1124 (1969); (b) R. E. Graf as quoted by N. A. Clinton and C. P. Lillya, *J. Amer. Chem. Soc.*, **92**, 3065 (1970).

(3) A. N. Nesmeyanov, K. N. Anisimov, and G. K. Magomedov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 715, 959 (1970).

(4) Evidence for existence of this type of cation has been described recently: R. E. Graf and C. P. Lillya, submitted for publication.

(5) (a) H. C. Brown, G. Marino, and L. M. Stock, *J. Amer. Chem. Soc.*, **81**, 3310 (1959); (b) H. C. Brown and G. Marino, *ibid.*, **81**, 5611 (1959); (c) G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *ibid.*, **86**, 2203 (1964).

(6) *Cf.* G. F. Emerson and R. Pettit, *ibid.*, **84**, 4591 (1962).

(7) Nesmeyanov, *et al.*,[3] have commented that the 2,3-dimethylbutadiene derivative is significantly more reactive than **1** but give no quantitative estimate of the difference or experimental basis for their conclusion.