(CDCl$_3$) δ 3.52 (1 H, s, COCHN(CH$_3$)CO); 87% after purification[19a]], which was transformed (HCOOMe–NaOMe–benzene) into a mixture of **17**[7] and **18**,[7] the former being readily converted to the latter (diazomethane). The oily compound **18** (80% from **16** after purification[19a]) was treated with *n*-butyl mercaptan and 10-camphorsulfonic acid in benzene giving oily **19**[7] (93% after purification[19a]), which on treatment with lithium dimethylcopper[20] in ether (−25°, 3 hr) gave **20**[7,8b,21] as an oil [ir (CHCl$_3$) 1730 (br), 1680 cm^{-1}; nmr (CDCl$_3$) δ 0.92 (6 H, d, J = 6.0 Hz, CH(CH_3)$_2$); 94% after purification[19b]]. Isomerization of **20** was effected by sodium hydride in glyme (reflux, 3 hr under nitrogen) affording a mixture of **20** and **21** (ratio 1:1), which was separated[22a] to give **21**,[7,8a,b,23,24] mp 146–147.5° [ir (CHCl$_3$) 1735, 1717, 1678 cm^{-1}; 50% based on reacted **20**]. Reduction of **21** with ethanolic sodium borohydride followed by acidification and subsequent purification[22b] afforded (±)-oxodendrobine (**2**),[7,8a,b,23] mp 182.5–183.5° (71%). Treatment of **2** with triethyloxonium fluoroborate in methylene chloride followed by reduction[25] of the resulting imino ether (NaBH$_4$–glyme) yielded an oily product forming a complex with boron; purification[19c] followed by passing the pyridine solution through a column of the anion exchange resin Amberlite IR-4B afforded (±)-dendrobine (**1**),[7,8a,b] mp 128–130° (61%), spectroscopically (ir, nmr, mass spectrum) and chromatographically identical with natural dendrobine.

[19] By preparative tlc on silica gel with CHCl$_3$–MeOH: (a) 95:5; (b) 97:3; (c) 90:10.

[20] R. M. Coates and R. L. Sowerby, *J. Amer. Chem. Soc.*, **93**, 1028 (1971).

[21] The stereochemistry at C-5 was secured to be retained in the derivatives **10–20** by chemical and/or nmr spectral evidence.

[22] By preparative tlc on aluminum oxide with (a) 1:1 EtOAc–C$_6$H$_6$; (b) 1:1 EtOAc–CHCl$_3$.

[23] Proved to be identical with the corresponding compound[3] prepared from natural **1** by spectral (ir, nmr, mass spectrum) and tlc comparison.

[24] Stereochemistry at C-4 and C-5 of **21**, a derivative of dendrobine, was rigorously established in the structural studies[3] of dendrobine, in connection with the stereochemistry of methyl oxodendrobinate **22** secured by extensive nmr spectral analysis.

[25] R. F. Borch, *Tetrahedron Lett.*, 61 (1968).

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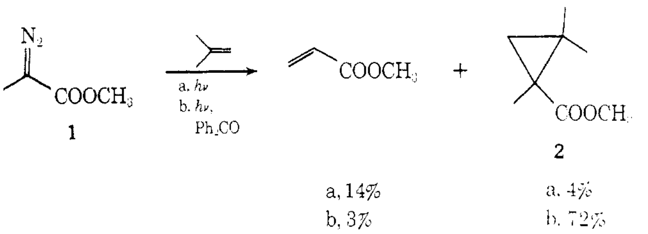
Suppression of Intramolecular Rearrangements of Carbenes. Methylcarbomethoxycarbene and Cyclopropylcarbomethoxycarbene[1]

Sir:

Although the most general synthesis of cyclopropanes utilizes the intermolecular addition of carbenes to olefins,[2] alkylcarbenes are virtually useless as cyclopropane precursors. Typically, intramolecular reactions, and especially insertions into carbon–hydrogen bonds, prevail over all intermolecular reactions. It seemed to us that triplet carbenes might avoid this problem. The suppression of the Wolff rearrangement in aliphatic diazo ketones had been previously noted,[3] and it had been pointed out by Moritani, Yamamoto, and Murahashi[4] that hydrogen or alkyl migrations to triplet carbenes must mimic the unknown[5] 1,2 shift in free radicals.

Accordingly, we have examined the direct and photosensitized photolyses of methyl diazopropionate (**1**).[6] As expected, the direct irradiation of **1** in isobutylene gave only 4% of adduct **2**, the major product being methyl acrylate.[7] By contrast, the benzophenone-sensitized decomposition of **1** led to **2** in 72% yield, with only 3% of the acrylate being formed.

cis- and *trans*-2-butene gave 10 and 6% adducts on direct irradiation.[8] These yields could be increased to 50 and 46%, respectively, by photosensitized decomposition of **1**.[8a] Methyl acrylate was decreased from *ca.* 27 to 3%. Products of abstraction of hydrogen were unimportant in the reactions with isobutylene and the 2-butenes.



In 1968, workers in Japan,[4] elaborating on the previous work of Overberger and Anselme,[9] studied the irradiation of phenylmethyldiazomethane. Here, sensitized decomposition was found to decrease the amount of hydrogen shift to give styrene from 7 to 1.7%, but no significant change could be found in the amount of intermolecular reaction to give cyclopropanes. The major change noted was the increased formation of acetophenone. We see no conflict between our work, in which we see dramatic increases in cyclopropane formation, and the previous. There is a growing conviction that a facile equilibrium exists between singlet and triplet phenylcarbenes.[10] In the case of phenylmethylcarbene, the major reaction of the triplet is apparently with adventitious oxygen, with the singlet forming most of the styrene and cyclopropanes.

In contrast to the 1,2-hydrogen migration, rearrangements of the cyclopropylcarbinyl radical are well known.[11] If it is the reluctance to undergo radical-like rearrangements that deters intramolecular reactions of triplet carbenes, a change of alkyl group from methyl to cyclopropyl should result in decreased deterrence. Ac-

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[1] Support for this work from the National Science Foundation through Grants GP-12759 and GP-30797X is warmly acknowledged.

[2] W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

[3] M. Jones, Jr., and W. Ando, *J. Amer. Chem. Soc.*, **90**, 2200 (1968).

[4] I. Moritani, Y. Yamamoto, and S.-I. Murahashi, *Tetrahedron Lett.*, 5697 (1968).

[5] W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

[6] M. B. Sohn, M. Jones, Jr., M. E. Hendrick, R. R. Rando, and W. von E. Doering, *Tetrahedron Lett.*, 53 (1972).

[7] All new compounds gave appropriate nmr and ir spectra and consistent elemental analyses.

[8] A report of the direct decomposition of **1** in the 2-butenes can also be found in the thesis of R. R. Rando, Yale University, New Haven, Conn., 1967.

[8a] Note Added in Proof. A determination of the degree of nonstereospecificity was precluded by the apparent photoisomerization of the adducts.

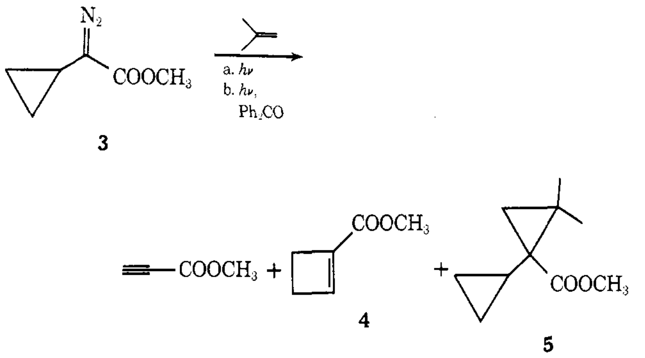
[9] C. C. Overberger and J.-P. Anselme, *J. Org. Chem.*, **29**, 1188 (1964).

[10] G. L. Closs, *Top. Stereochem.*, 3, 193 (1968).

[11] C. Walling, "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 407.

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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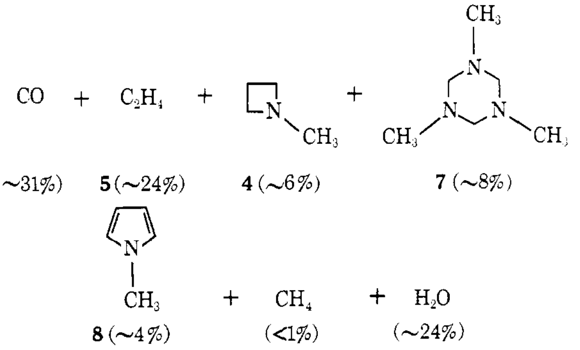
Photolysis of *N*-Methyl-2-pyrrolidone

Sir:

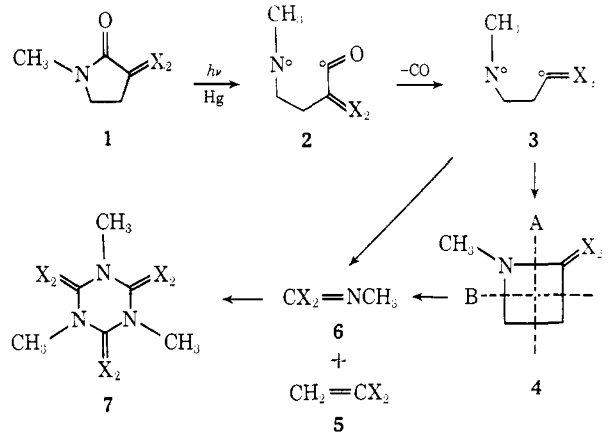
The photochemistry of carbonyl compounds, especially ketones and aldehydes, has been the subject of intensive investigation for some time.[1,2] One of the areas that has received relatively little attention is the photochemistry of lactams and, while there have been studies carried out on the solution 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).