variable changed is γ_N. Thus the pmr/dmr line-width ratio is expected to be close to the value of $\sim$42 predicted by theory. It is apparent from the table that this ratio is not always realized. In order to test for the effects of changes in concentration and possible saturation, pmr and dmr spectra of the Mn(III) complex were measured on samples ranging from 0.08 to 0.40 M and at several radiofrequency power levels. The resulting line widths agree within about 10%. Deviations from the theoretical line-width ratio were found earlier for solutions of paramagnetic metal ions in H_2O and D_2O.[6] These results imply that other factors, presently undetermined, affect the relaxation times of nuclei in paramagnetic environments.

Although the pmr/dmr ratios in Table I are not generally in agreement with theory, the present results do indicate a gain in resolution upon replacing protons by deuterons in paramagnetic molecules. We hope this will allow extension of isotropic shift studies to metal ions having relatively long τ_s. The improvement in resolution is most noticeable for Cr(acac)$_3$; both the CH_3 and C–H resonances are clearly seen in the dmr spectrum. The C–H signal is not apparent in the pmr spectrum. Another advantage of dmr over pmr for paramagnetic systems is that selective deuteration allows unambiguous signal assignments and avoids interference from resonances of nuclei at other sites (not deuterated). Furthermore, spectra are less likely to be complicated by spin–spin coupling, since $J_{DD} < J_{DH} < J_{HH}$.

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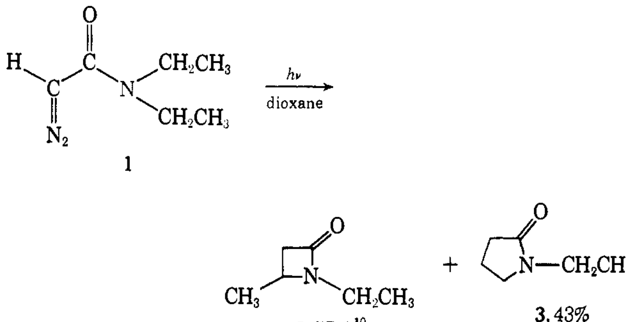
Received August 1, 1970

Conformational and Solvent Effects on Carbene Reactions[1]

Sir:

Carbalkoxycarbenes, generated by the photolysis of the parent diazo esters, undergo facile intermolecular C–H insertion and double bond addition reactions in hydrocarbon solvents.[2,3] Curiously, the intramolecular counterparts of these reactions, which would generate lactones, are not realized. For example, the photolytic decomposition of allyl diazoacetate in cyclohexane gives rise to allyl cyclohexylacetate as the sole product.[4] One only starts to see lactone formation when the alkoxy portion of the diazo ester is exceptionally bulky. Photolysis of *tert*-butyl diazoacetate in cyclohexane affords 9.5% γ,γ-dimethylbutyrolactone along with 90.5% *tert*-butyl cyclohexylacetate.[5] It would appear that the dominant factor in these reactions is a conformational one,[6] whereby the *O*-alkyl moiety of the diazo esters never achieves sufficient proximity to the divalent center, except in the bulky *tert*-butyl case, for intramolecular reactions to ensue. If this is indeed the case, we would expect *N,N*-dialkyl diazo amides to undergo principally intramolecular lactam formation upon photolysis, since one alkyl group must lie in close proximity to the divalent center as a consequence of the planar peptide bond. We herein report the results of a study of the photochemistry of *N,N*-diethyldiazoacetamide (**1**) and demonstrate a remarkable solvent effect on its reactions.

N,N-Diethyldiazoacetamide (**1**) was prepared by condensing *p*-nitrophenyl diazoacetate with diethylamine in the usual manner.[7] After purification on Woelm activity grade IV alumina, **1** was obtained as a viscous yellow oil which exhibited strong infrared absorption ($CHCl_3$) at 4.69 and 6.2 μ and nmr absorption ($CDCl_3$) at τ 4.9 (s) of relative area 1, 6.7 (q)[8] of relative area 4, and 8.8 (t)[8] of relative area 6. Photolysis[9] of 270 mg of the diazoamide in 15 ml of dry, distilled *p*-dioxane led to the recovery of 205 mg of a light yellow oil after the removal of the dioxane. Vapor phase chromatography of this material on 5 ft × $^1/_4$ in. 5% Carbowax 20M on Chromosorb W (60–80 mesh) at 150° column temperature showed that two major products had formed accounting for 97% of the total amount. The product with the longer retention time proved to be 1-ethyl-2-pyrollidinone (**3**) by comparison with authentic material.[11] The other product proved to be 1-ethyl-4-methyl-2-azetidinone (**2**). This β-lactam exhibited carbonyl absorption in the infrared ($CHCl_3$) at 6.28 μ,[12] nmr[13] absorption ($CDCl_3$) at τ 6.3 (m) of relative area 1, 6.8 (q) of relative area 2, 7.2 (m) of relative area 1, 7.4 (m) of relative area 1, 8.7 (d) of relative area 3, and 8.9 (t) of relative area 3. The mass spectrum of the colorless oil **2** revealed the expected molecular ion at



1

2, 57%[10]

3, 43%

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(1) This work was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society (No. 1489-G1).

(2) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **78**, 4947 (1956); **83**, 1989 (1961).

(3) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, Chapter 6.

(4) W. Kirmse and H. Dietrich, *Chem. Ber.*, **98**, 4027 (1965).

(5) W. Kirmse, H. Dietrich, and H. W. Bucking, *Tetrahedron Lett.*, **19**, 1833 (1967).

(6) F. Kaplan and G. K. Meloy, *J. Amer. Chem. Soc.*, **88**, 950 (1966).

(7) H. Chaimovich, R. J. Vaughan, and F. H. Westheimer, *ibid.*, **90**, 4088 (1968).

(8) The fact that a single methylene quartet and a single methyl triplet are observed probably means that rotation about the peptide bond is rapid at room temperature relative to the nmr time scale in diazoamides.

(9) Photolyses were carried out through Pyrex vessels using G.E. sunlamps with external water cooling. The reactions were run until the diazo stretching absorption (4.69 μ) was no longer visible in the infrared spectrum (usually 8–10 hr).

(10) Relative per cent yields were obtained from the vpc trace after suitable corrections for electrical conductivity and statistical factors were made. The absolute overall yield is 94% based on diazo amide.

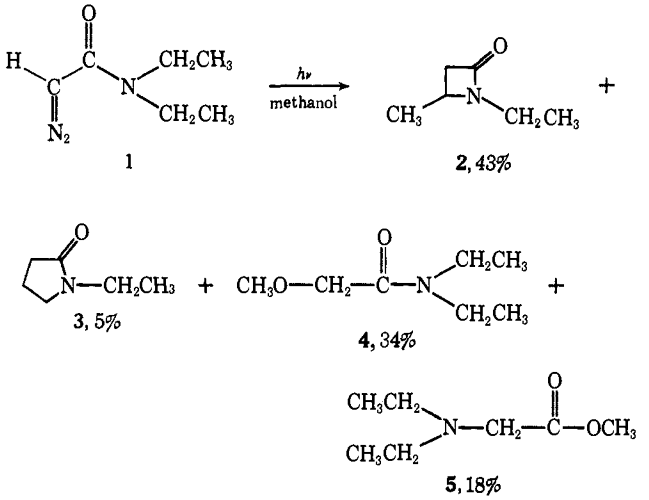
(11) Infrared and nmr spectra were compared along with vpc retention times.

(12) An amide carbonyl absorption this high is quite indicative of a β-lactam moiety; see L. M. Bellamy, "Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958, p 214.

(13) The nmr spectrum of the compound was quite similar to analogous β-lactams in K. D. Barrow and M. T. Spotswood, *Tetrahedron Lett.*, 3325 (1965).

113 in addition to showing a cracking pattern uniquely ascribable to a four-membered β-lactam ring.[14] A similar mode of β-lactam formation was reported by Corey[15] in the synthesis of a penicillin derivative. Quite strikingly, no intermolecular insertion into the dioxane was observed.[16] This coupled with the exclusive formation of β and γ lactams (**2** and **3**) is entirely consistent with the idea that the dominant force in these reactions is a conformational one. Of course, the results obtained from the photolysis of diazo esters, where intermolecular products are exclusively formed, are diametrically opposed to the ones reported here.

When diazo esters are photolytically decomposed in hydroxylic solvents, such as alcohols, the formation of intermolecular C–H insertion products is all but abolished at the expense of Wolff rearrangement and O–H insertion.[7,17] With this in mind, we photolyzed[18] **1** in methanol to see what effect this would have on the intramolecular insertion processes. Remarkably, the yield[19] of β-lactam **2**[20] was little affected, whereas the formation of γ-lactam **3** was nearly nullified. The amide **4** is the O–H insertion product and the ester **5** arises by addition of methanol to the Wolff-rearranged product. Both structures were proved by comparison with authentic materials. The suppression of γ-lactam **3** formation finds analogy in the suppression of intermolecular C–H insertion when ethyl diazoacetate is photolyzed in methanol[7] or isopropyl alcohol.[17]



1

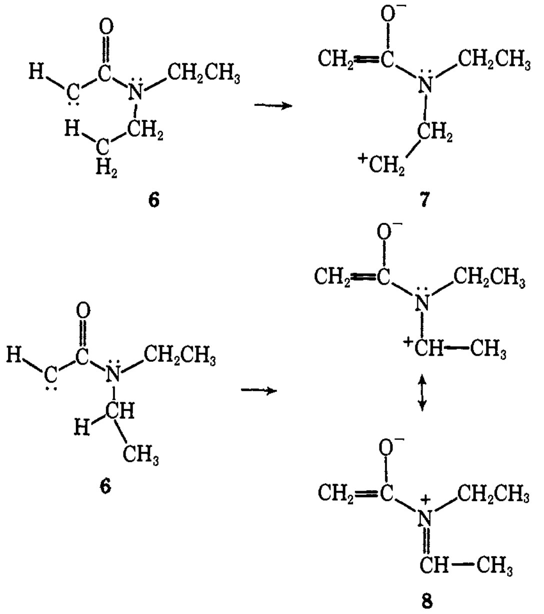
2, 43%

3, 5%

4, 34%

5, 18%

The fact that β-lactam formation is not markedly reduced requires that the mechanism of its formation be different from that leading to γ-lactam. One would expect the charge separation developed in their respective transition states to be markedly different. Structures such as **7** should *not* be important contributors to the γ-lactam transition state, whereas strctures such as **8** should be important contributors to the β-lactam one.[21]


6 → **7**

6 → **8**

We argue, then, that the β-lactam transition state, having developed greater charge separation, is differentially stabilized by the small, polar methanol molecules and hence able to compete with Wolff rearrangement and O–H insertion.

In attempting to utilize carbalkoxycarbenes to label the aliphatic residues of proteins, Westheimer[22] found that most of the carbene was "wasted" by Wolff rearrangement and O–H insertion into water. Our results are in accord with these findings since even the conformationally favorable formation of γ-lactam **3** was nearly wiped out in a hydroxylic solvent. This suggests that C–H insertion will be circumvented no matter how close the carbene is generated to the aliphatic site, as long as water is in its vicinity.

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Received August 21, 1970

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(14) H. E. Audier, M. Fetizon, H. B. Kagan, and J. L. Luche, *Bull. Soc. Chim. Fr.*, 2297 (1967); M. Fisher, *Chem. Ber.*, **101**, 2669 (1968).

(15) E. J. Corey and A. M. Felix, *J. Amer. Chem. Soc.*, **87**, 2518 (1965).

(16) Demonstrated by the observation that no additional peaks were observable on the vpc and that the nmr of the crude product (before chromatography) showed no signals other than those accountable for by the β- and γ-lactams.

(17) O. P. Strausz, T. DoMinh, and H. E. Gunning, *J. Amer. Chem. Soc.*, **90**, 1660 (1968).

(18) Photolyses were carried out as before.[9] In one example 170 mg of **1** was photolyzed in 10 ml of methanol until the diazo group stretching absorption was no longer visible in the infrared spectrum. Careful fractional distillation of the solution led to the recovery of 155 mg of solvent-free product as a yellow liquid.

(19) After vapor phase chromatography on 5 ft × $^{1}/_{4}$ in. 5% Carbowax 20M on Chromosorb W (60–80 mesh) at 150° column temperature. All four products could be cleanly separated under these conditions. Per cent yields shown are corrected for differences in electrical conductivity and the β/γ lactam ratio has also been corrected for the statistical factor. The yields shown in the figure are relative. The absolute overall yield is 90% based on diazoamide.

(20) It is noteworthy that the photolysis of *N*-methyldiazoacetamide in water[7] gives rise to OH insertion and Wolff rearrangement products but no β-lactam, which is entirely consistant with the importance of conformational factors in these reactions. We would expect monoalkyl diazoamides to behave photochemically like diazo esters.

(21) For ease of exposition the hydrogen atoms are shown fully transferred in the β- and γ-lactam transition state contributors. A more precise description of the transition states would probably require the hydrogens to be only partially transferred with concomitant partial charge separation.

(22) J. Shafer, P. Baranowsky, R. Laursen, F. Finn, and F. H. Westheimer, *J. Biol. Chem.*, **241**, 421 (1966).