$$g = \frac{\epsilon_L - \epsilon_R}{\frac{1}{2}(\epsilon_L + \epsilon_R)} = \frac{\Delta\epsilon}{\epsilon}$$

ϵ is the mean decadic molecular extinction coefficient. As theoretically expected and experimentally confirmed, circular dichroism has its counterpart in emission (circular polarization of luminescence; CPL).[1] Again a dissymmetry factor can be defined

$$g_{\text{lum}} = \frac{I_L - I_R}{\frac{1}{2}(I_L + I_R)} = \frac{\Delta I}{I}$$

I_L (I_R) is the quantity of emitted left (right) circularly polarized light in relative quanta per frequency interval.

Measurement of CD requires one of the two optical isomers in the pure state, whereas measurement of CPL offers a possibility to escape from this restriction. Upon irradiation of a racemic mixture with, for instance, left circularly polarized light one optical isomer will be preferentially excited (with a factor $(1 + g/2)/(1 - g/2)$ as compared to the other isomer). Consequently the luminescence will exhibit a dissymmetry factor

$$g_L = \frac{I_L^L - I_R^L}{\frac{1}{2}(I_L^L + I_R^L)} = \frac{1}{2}g(\lambda_1)g_{\text{lum}}(\lambda_2)$$

(since g and g_{lum} vary with wavelength, g_L will depend upon the wavelength of excitation (λ_1) and observation (λ_2)).

If the excitation light is right circularly polarized we find

$$g_R = \frac{I_L^R - I_R^R}{\frac{1}{2}(I_L^R + I_R^R)} = -\frac{1}{2}g(\lambda_1)g_{\text{lum}}(\lambda_2)$$

Monochromatic circularly polarized light was obtained from a 450-W Xenon lamp, Cary double-prism monochromator, and circular polarizer (calcite Glan prism; quartz quarterwave plate). The luminescence was observed perpendicularly to the excitation beam. By means of a circular analyzer, consisting of a rotating quartz retardation plate followed by a polaroid polarizer, phase-sensitive detection methods could be used to determine $I_L - I_R$. Simultaneously $\frac{1}{2}(I_L + I_R)$ was recorded. The measuring equipment was calibrated by placing solutions of well-known optically active compounds between a luminescing nonoptically active compound and the circular analyzer and measuring their CD. It appeared that $(I_L - I_R)/[\frac{1}{2}(I_L + I_R)]$ could be determined within 1×10^{-3}. A solution of racemic *trans*-β-hydrindanone in isooctane (10^{-2} *M*) irradiated with 317-nm light yielded $gg_{\text{lum}} = +4 \times 10^{-3}$ (separate measurement of g at 317 nm, and g_{lum} as an average over the whole emission band yielded values of $+0.17$ and $+19 \times 10^{-3}$, respectively, for the + isomer, so that their product gg_{lum} equals $+3.2 \times 10^{-3}$).[2]

If one would know beforehand that g is equal to g_{lum}, this method would allow a direct determination of the rotational strength of an absorption band of an optically active molecule without actually isolating it from a racemic mixture. In many cases g will be different from g_{lum} which complicates the theoretical interpretation. Irrespective of this limitation one can obtain the form of the g curve by exciting at several wavelengths (as one can find the form of the g_{lum} curve upon irradiation at a fixed wavelength). The method may also be of practical value in ascertaining whether a compound that does not show ORD or CD is a racemic mixture or a *meso* structure. Another possible application is the study of chiral conformations of systems whose lifetimes are on the one hand long enough to prevent racemization in the excited state but on the other hand too short to permit resolution in the ground state.

Finally, transfer of excitation energy between one optical isomer and the other or excimer formation between them will decrease the effect of the preferential excitation. These effects may therefore be detected by this technique because the observed g_L will be lower than the value calculated with the above-mentioned equation.

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Received April 7, 1969

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(1) C. A. Emeis, Ph.D. Thesis, University of Leiden, 1968; C. A. Emeis and L. J. Oosterhoff, *Chem. Phys. Letters*, **1**, 129 (1967).

(2) The observed luminescence may be the fluorescence of an excimer,[3] in which case the above-mentioned expressions for g_L and g_R need not apply. No deviation from them could be detected with the presently available instrument.

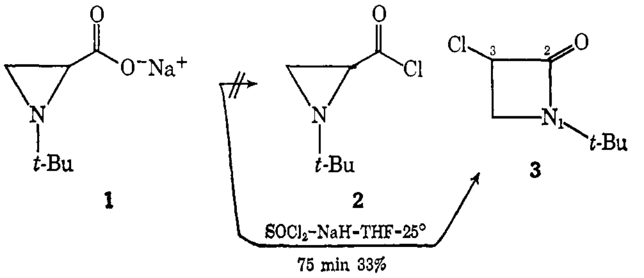
(3) M. O'Sullivan and A. C. Testa, *J. Am. Chem. Soc.*, 90, 6246 (1968).

A New Route to β-Lactams

Sir:

Elucidation of the penicillin and cephalosporin structures has stimulated a continuing interest in the development of new synthetic routes to biologically active β-lactams.[1] We wish to report that entry into functionally substituted β-lactams can be achieved by ring expansion of the aziridine ring.

Reaction of **1** with $SOCl_2$ yielded a neutral compound ($C_7H_{12}NOCl$)[2] instead of the usual acid chloride (**2**). We have assigned the 1-*t*-butyl-3-chloro-2-azetidinone structure (**3**) to this compound on the basis of its physical and spectral [*e.g.*, ir (liquid film) 1760 cm^{-1} (C═O)] properties. Additional confirmation for the β-lactam structure was obtained from the Zn–EtOH reduction[3] of **3** to 1-*t*-butyl-2-azetidinone.[4]



1 **2** **3**

Some initial observations concerning the scope of this reaction are also relevent to defining the reaction mechanism. For example, the conversion of **1** to **3** could also be affected by oxalyl chloride in benzene with (29%) or without (26%) added Et_3N. The sim-

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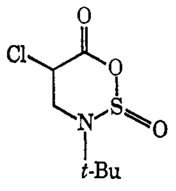
(1) A. K. Bose, G. Spiegelman, and M. S. Manhas, *J. Am. Chem. Soc.*, **90**, 4506 (1968); E. J. Corey and A. M. Felix, *ibid.*, **87**, 2518 (1965).

(2) Satisfactory elemental and spectral (nmr, ir, and mass) analyses were obtained for all compounds unless otherwise indicated.

(3) *Cf.* I. L. Knunyants and N. P. Gambaryan, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 834 (1957); *Bull. Akad. Sci. USSR, Div. Chem. Sci.*, 855 (1957).

(4) This material was shown identical with that prepared (7% yield) from the reaction of *t*-butylaminopropionic acid with $SOCl_2$ and Et_3N.

ilar behavior of both $SOCl_2$ and oxalyl chloride suggests that both reagents produce a common intermediate and argues against formation of intermediates such as **4** and **5**.[5] The previously established stability of various



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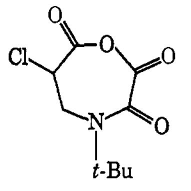

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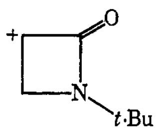
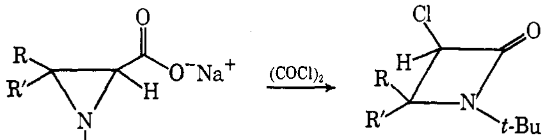


6

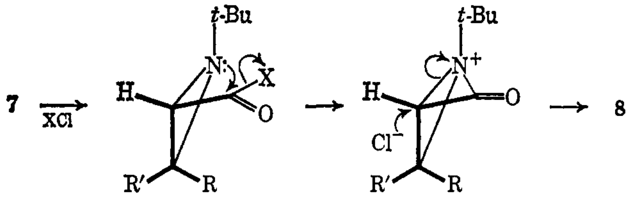
model aziridines toward acid halides and protons in the presence of Et_3N also excludes ring opening of some aziridinium species to an acyclic prescursor of **3**.[7] The possible intervention of symmetrical carbonium ion **6** can be ruled out by the stereospecific[8] conversion of **7a** and **7b** to **8a** and **8b**, respectively.[9]



7a, R = CH_3; R′ = H
b, R = H; R′ = CH_3

8a, R = CH_3; R′ = H (79%)[10]
b, R = H; R′ = CH_3 (63%)

We believe that these results can only be explained in terms of ionization of mixed anhydride **9** to give the novel bicyclic ion **10**.[11] Capture of this remarkably strained intermediate by Cl^- should occur in the manner shown to give **8** with the correct stereochemistry.



9 **10**

X = SOCl or COCOCl

The mild conditions, the good yields, and the stereospecificity make this ring expansion a potentially useful route to β-lactams. Further work is now in progress on the extension of this rearrangement to the synthesis of more complex molecules. Additional chemistry of **10** is also being studied.

Acknowledgment. Support of this research by National Science Foundation Grants GP-5531 and GP-8044 is gratefully acknowledged.

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Received May 29, 1969

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(5) The conversion of either intermediate to product under the reaction conditions seems unlikely.[6]

(6) *Cf.* J. A. Deyrup and C. L. Moyer, *J. Org. Chem.*, **34**, 175 (1969).

(7) C. L. Moyer, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1968; J. A. Deyrup and C. L. Moyer, *Tetrahedron Letters*, 6179 (1968).

(8) Stereochemistry was based on the relative (*cis* > *trans*) magnitude of J_{vic}.

(9) The formation of different products from **7a** and **7b** adds nonspectral evidence for the position of the Cl group.

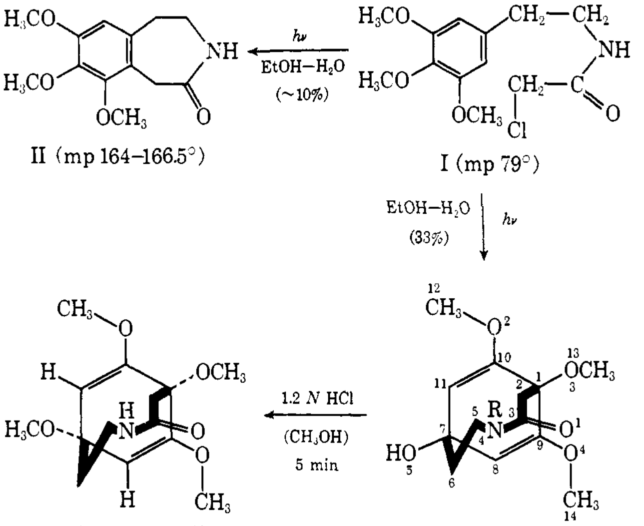
(10) Although ample spectral data were obtained for this structure, a satisfactory elemental analysis could not be obtained for **8a**.

(11) Although intermediacy of 1-azabicyclobutonium cations has been postulated previously,[7] the presence of the carbonyl group in a three-membered ring would be expected to contribute considerable added strain energy to **10**.

Photocyclizations of Pharmacodynamic Amines. III. Three-Dimensional Structure of 7-Hydroxy-1,9,10-trimethoxy-4-azabicyclo[5.2.2]undeca-8,10-dien-3-one from Mescaline[1]

Sir:

The presence of one or two methoxy substituents has greatly influenced the direction of cyclization and the nature of the products resulting from deep-seated rearrangements in the photolysis of N-chloroacetylphenethylamines.[2,3] The long-sought-after products of the photolysis of N-chloroacetylmescaline (I) have now finally been isolated and crystallized. One product, $C_{13}H_{17}NO_4$,[4] is 7,8,9-trimethoxy-1,2,4,5-tetrahydro-3(3H)-benzazepin-2-one (II), the first example of such a ring closure in the mescaline series in the absence of *ortho* or *para* activation by a phenolic hydroxyl group. The second photoproduct, after extensive purification by column chromatography over silica gel, was obtained as colorless prisms from methanol–ether in yields approaching 35%. The compound which had only end absorption in the uv had the composition $C_{13}H_{19}NO_5$. It was characterized by an acetylation product IV, colorless prisms, mp 188–189.5°.



II (mp 164–166.5°)

I (mp 79°)

V (mp 176–179°)

III, R = H (mp 230–232°)
IV, R = Ac (mp 188–189.5°)

An X-ray diffraction analysis of a single crystal established the structure and configuration III of this photoproduct. The compound crystallizes in the *orthorhombic space group Aba2* which does not have a

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(1) Presented in part at the Annual Meeting of the Japanese Pharmaceutical Chemistry Society, Nagoya, April 4–6, 1969.

(2) O. Yonemitsu, T. Tokuyama, M. Chaykovsky, and B. Witkop, *J. Am. Chem. Soc.*, **90**, 776 (1968).

(3) O. Yonemitsu, Y. Okuno, Y. Kanaoka, I. Karle, and B. Witkop, *ibid.*, **90**, 6522 (1968).

(4) Correct analyses for C, H, and N were obtained for all compounds reported.