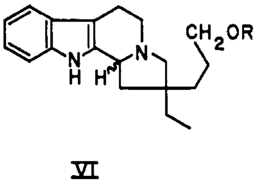
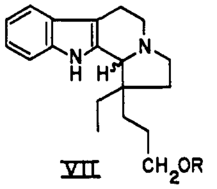
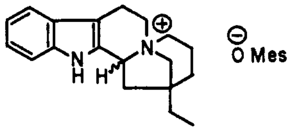
bromide in dichloromethane at 0° to provide the amino alcohol (VI, R = H) which still retained the normal indole ultraviolet spectrum while the nmr spectrum indicated a complete absence of the typical benzyl ether proton signals mentioned above. The molecular formula, $C_{19}H_{26}N_2O$, was again established by high-resolution mass spectrometry (Found: mol wt, 298.204. Calcd: mol wt, 298.204) and the mass spectrum also indicated fragments at *m/e* 184, 170, 156, etc., as mentioned above.


VI


VII


VIII

The total synthesis of *dl*-quebrachamine was completed when the quaternary mesylate (VIII), formed directly from the reaction of the amino alcohol with methanesulfonyl chloride in pyridine, was reduced with sodium and liquid ammonia.[13,14] The reaction product was identical with an authentic sample of (−)-quebrachamine obtained from natural sources (infrared, thin layer chromatography, mass spectrometry).

This synthesis also completes a total synthesis of *dl*-aspidospermidine.[4] Since there is little doubt that tryptamine derivatives bearing functional groups (OCH_3, for example) on the aromatic ring will react similarly, the above sequence can be extended to other Aspidosperma alkaloids.

The obvious extension of this synthesis to the Vinca alkaloids, the dihydrocleavamine series, and, in turn, to the Iboga alkaloids is now under investigation.

Acknowledgment. Financial aid from the National Cancer Institute of Canada and the National Research Council of Canada is gratefully acknowledged.

(13) E. Wenkert, S. Garratt, and K. G. Dave, *Can. J. Chem.*, **42**, 489 (1964).

(14) J. P. Kutney, E. Piers, and T. Inaba, unpublished results.

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β-Lactams Containing an Exocyclic Double Bond[1]

Sir:

We wish to report that symmetrically and unsymmetrically substituted allenes[2] react with chlorosulfonyl isocyanate (CSI)[3] to form β-lactams containing an exocyclic double bond and 2-carboxamido-1,3-butadiene derivatives.

In general, the allenes are added slowly to CSI in ether solution, after which the mixture is added to ice and the whole extracted with water. Thus, 3-methyl-1,2-butadiene (**1**),[4] on treatment with CSI, gave 1-chlorosulfonyl-3-methylene-4,4-dimethyl-2-azetidinone (**3**, 21%) from the ether solution and, from the aqueous extract, 2-carboxamido-3-methyl-1,3-butadiene (**4**, 36%). A third, as yet unidentified, product was obtained in 22% yield.[5] Compound **3** was obtained as white plates from pentane, mp 51–52°; $\lambda_{max}^{CCl_4}$ 5.51 μ (C=O). *Anal.* Found: C, 34.61; H, 4.03; N, 6.80. The nmr spectrum (CCl_4) displayed absorptions at δ 1.79 (6 H, singlet), 5.57, and 6.05 (2 H, two identical vinyl doublets, J = 2.5 cps). Reduction of **3** with benzenethiol and pyridine in acetone[6] led to 3-methylene-4,4-dimethyl-2-azetidinone (**5**, 55%) as long white needles from pentane, mp 64–65° (sublimed 50° (1 mm)); $\lambda_{max}^{CS_2}$ 5.63 and 5.69 μ (C=O);[7] $\lambda_{max}^{CHCl_3}$ 3.24 μ (=CH_2, Raman). *Anal.* Found: C, 65.15; H, 8.42; N, 12.59. Ozonolysis of **3** and **5** furnished formaldehyde, identified as its 2,4-DNP derivative. Butadiene **4** was obtained as long white needles from ether–petroleum ether (bp 30–60°), mp *ca.* 70° (rapid heating); λ_{max}^{KBr} 6.09 (C=O), 6.18, and 6.32 μ; $\lambda_{max}^{CH_3OH}$ 223 $m\mu$ (ϵ 7800). *Anal.* Found: C, 64.90; H, 8.24; N, 12.27. The nmr ($CDCl_3$) consisted of absorptions at δ 1.92 (3 H, multiplet), 5.11 (2 H, multiplet, β =CH_2), 5.28, 5.52 (2 H, two unresolved singlets, peak width at half-height 4 cps, α =CH_2), and *ca.* 6.30 (2 H). Treatment of **4** with maleic anhydride yielded the Diels–Alder adduct, white plates, mp 160–161°.[8]

The β-lactam **5** was identified by hydrolytic cleavage to the unsaturated amino acid hydrochloride (**6**),[8] reduction of which produced 3-amino-2,3-dimethylbutanoic acid hydrochloride (**7**).[8,9] The identity of butadiene **4** was established by stepwise reduction to

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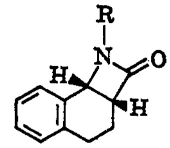
(1) For a review of available methods of β-lactam synthesis, see J. C. Sheehan and E. J. Corey, *Org. Reactions*, **9**, 388 (1958). Two new syntheses have recently been reported: E. J. Corey and A. M. Felix, *J. Am. Chem. Soc.*, **87**, 2518 (1965); R. B. Woodward, K. Heusler, J. Gosteli, P. Naegeli, W. Oppolzer, R. Ramage, S. Ranganathan, and H. Vorbrüggen, *ibid.*, **88**, 852 (1966).

(2) A recent review of allene chemistry is available: A. A. Petrov and A. V. Fedorova, *Russ. Chem. Rev.*, **33**, 1 (1964).

(3) H. Ulrich, *Chem. Rev.*, **65**, 369 (1965), summarizes the chemistry of CSI to July 1964. We have recently reported on the reaction of 1,2-dihydronaphthalene with CSI to prepare i, and therefrom, ii [E. J. Moriconi and P. H. Mazzocchi, *J. Org. Chem.*, **31**, 1372 (1966)]. CSI is now commercially available from American Hoechst Corp., New York, N. Y.


i, R = SO_2Cl
ii, R = H

(4) W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, **20**, 95 (1955).

(5) This compound seems to be an adduct of two equivalents of CSI with one of **1**.

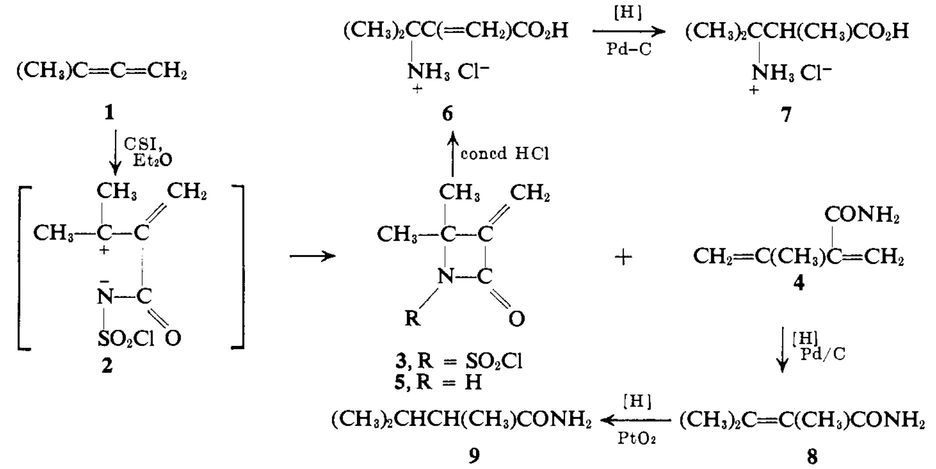
(6) R. Graf, *Ann.*, **661**, 111 (1963).

(7) The infrared spectrum of **5** showed marked and reversible changes with concentration suggestive of a monomer ⇄ (dimer) ⇄ polymer equilibrium, probably involving intermolecular hydrogen bonding between N—H and O=C bonds. Thus in dilute solution, the main, monomeric C=O peak appeared at 1777 cm^{-1}, with a weak secondary at 1757 cm^{-1} (dimer or polymer C=O); with increasing concentration these intensities reversed. Similarly the N-H stretching band of the monomer at 3430 cm^{-1} is progressively displaced at higher concentration by the typical broad N-H stretching band at 3240 cm^{-1} of the bonded species.

(8) Satisfactory elemental analytical data and nmr, ultraviolet, and infrared spectra have been obtained for this compound.

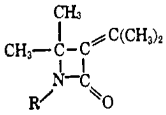
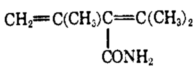
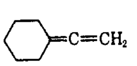
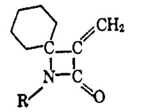
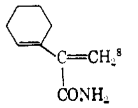
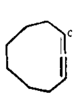
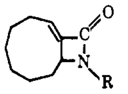
(9) Compound **7** was identical by all the usual criteria with the acid hydrolysis product of 3,4,4-trimethyl-2-azetidinone.[6]

Scheme I



the known 2,3-dimethylcrotonamide (**8**),[10,11] and finally to the known 2,3-dimethylbutanamide (**9**)[13] (see Scheme I).

Table I. Products and Yields of CSI Addition to Allenes

Allene	Products			
	β-Lactam	% yield	Diene	% yield
$(CH_3)_2C=C=C(CH_3)_2$		R = SO_2Cl[8] 73 R = H[8] 72[a]	 $CH_2=C(CH_3)C(CONH_2)=C(CH_3)_2$[8]	22
		R = SO_2Cl[8] 38 R = H[8] 68[a]		32
		R = SO_2Cl 89[b] R = H[8] 40[a]		

[a] Obtained by reduction of the N-chlorosulfonyl-β-lactam with benzenethiol and pyridine in acetone.[6] [b] Crude oil. [c] K. G. Untch, D. J Martin, and N. T. Castellucci, *J. Org. Chem.*, **30**, 3572 (1965).

The zwitterionic transition state **2** proposed is consistent with the two-step, 1,2-dipolar cycloaddition mechanism originally suggested by Graf.[6,14] The CSI adds predominantly to the central carbon of the allenic system[15] leading to the more stable, tertiary carbonium ion, which, after suitable rotation, receives additional stabilization as an allylic cation. The developing negative charge on the nitrogen atom in **2** is also stabilized by its two adjacent electronegative groups. Cyclization of **2** would lead to **3**, while proton transfer from C to N would produce **4**.

The results of CSI addition to three additional allenes are summarized in Table I.

Acknowledgment. We are grateful to Professor R. Norman Jones (National Research Council) for the determination and interpretation of the infrared and Raman spectra of **5**. This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grants AF-AFOSR-62-18 and -488-64.

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[10] E. J. Corey, *J. Am. Chem. Soc.*, **75**, 1163 (1953).

[11] This 1,4 reduction seems unlikely; more probably, 1,2 reduction of the terminal methylene group in **4** occurs initially to give 2-methylene-3-methylbutanamide (**10**) followed by isomerization to **8**. Significantly, the isomeric 1,2-reduction product (**11**)[10,12] did not isomerize under the reaction conditions.

$CH_3CH(CH_3)C(=CH_2)CONH_2$ **10** $CH_3C(=CH_2)CH(CH_3)CONH_2$ **11**

[12] Obtained by us as one of the CSI addition products to trimethylethylene.[6]

[13] C. D. Nenitzescu and I. Chicos, *Ber.*, **68**, 1584 (1935); also prepared by us *via* reduction (Pd-C) of **11**.

[14] A concerted mechanism has been shown to be disallowed in such cases by recently developed selection rules for such cycloaddition reactions [R. Hoffman and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965)].

[15] As has also been reported to occur in the oxymercuration of substituted allenes [E. F. Kiefer and W. L. Waters, Organic Division, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstracts, Paper K44].

Kinetic Studies of Group VI Metal Carbonyl Complexes. III. Substitution Reactions of Molybdenum Hexacarbonyl

Sir:

Recent kinetic studies[1] indicate that the substitution reactions of $Mo(CO)_6$ with phosphines and amines

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[1] H. Werner, *J. Organometal Chem.*, **5**, 100 (1966).