2-Benzoyl-10-(*p*-benzoylphenyl)-9-phenyl-9-acridanol (2k).—4,4′,4″-Tribenzoyltriphenylamine [1g, free (tlc) of mono- and dibenzoytriphenylamine impurity] was stirred with PPA (20 g) at 190–195° for 0.5 hr; a small amount of benzoic acid (identified by its infrared spectrum) sublimed. After cooling, water (~50 ml) was added, acid-insoluble material E (0.6–0.7 g, tlc showed negligible base 1g) was removed, and the filtrate was made alkaline to deposit a pale yellow solid (0.2 g) shown by its infrared and mass spectra to be a mixture of acridanols 2j and 2k. Product E was dissolved in glacial acetic acid (5 ml) and treated as for D above to provide crude acridanol 2k (0.2 g) which was purified by dissolving in benzene and adding petroleum ether (bp 80–100°) to afford a buff-colored solid, mp 115–120°.

Anal. Calcd for $C_{39}H_{27}NO_3 \cdot H_2O$: C, 81.37; H, 5.08; N, 2.43. Found: C, 81.70; H, 5.31; N, 2.46.

The mass spectrum showed a very weak parent peak at *m/e* 557, a weak peak at *m/e* 540 (M − OH), a weak peak at *m/e* 481 (M − C_6H_5 +1), a weak peak at *m/e* 464 (M − OH − C_6H_5 + 1), a base peak at *m/e* 436 (M − OH − C_6H_5CO + 1), and a medium peak at *m/e* 360 (M − OH − $C_6H_5COC_6H_4$ + 1).

A sample of acridanol 2k was prepared unambiguously by cyclization of 2,4′,4″-tribenzoyltriphenylamine (1f, 0.15 g) with PPA (5 g) at 120–125° for 0.5 hr. Addition of water (~100 ml) to the orange fluorescent solution gave a sparingly soluble gum which was separated by decantation and dissolved in glacial acetic acid (5 ml). The acid solutions were combined, warmed to dissolve the sparingly soluble acridanol 2k, filtered hot (charcoal), and made alkaline to afford crude 2k (0.18, ~70%) which was identical (infrared and mass spectra) with the rearrangement product of 1g. In concentrated sulfuric acid (1 ml) conversion of amine 1f (0.2 g) into acridanol 2k proceeded very slowly at 20° compared with the conversion amines 1c and 1i; reaction at 90° for 1 hr afforded base 2k in ~20% yield.

Deacylation of 4,4′,4″-Tribenzoyltriphenylamine (1g).—A mixture of the amine (1g, 0.3 g) and excess of triphenylamine (1 g) in PPA (10 g) was stirred at 190° for 0.5 hr. After addition of water and removal of acid-insoluble material, the green fluorescent filtrate was made alkaline to give 9,10-diphenyl-9-acridanol (2a, 0.25 g, 45% yield, based on complete deacylation of amine 1g) which showed no carbonyl absorption in its infrared spectrum.

Registry No.—1a, 16911-31-2; 1b, 16911-32-3; 1c, 16911-33-4; 1e, 16911-34-5; 1f, 16911-35-6; 1g, 1183-66-0; 1h, 1159-53-1; 1i, 16959-98-1; 1j, 16959-99-2; 4-benzoyldiphenylamine, 4058-17-7; 2a, 16911-37-8; 2b, 16911-38-9; 2c, 16911-39-0; 2d, 16911-40-3; 2e, 16960-00-2; 2f, 16960-01-3; 2g, 16911-41-4; 2h, 16911-42-5; 2i, 16911-43-6; 2j, 16911-44-7; 2k, 16911-45-8; 2l, 16911-46-9; 2m, 16911-47-0; 3, 16911-48-1; triphenylamine, 603-34-9.

Acknowledgment.—The author thanks Mr. A. E. L. D. Parker and Mr. A. J. Hodgkinson for assistance with some of the experimental work, Dr. S. Eggers for the mass spectra, and the South African Council for Scientific and Industrial Research for financial support.

The Reaction of Chlorosulfonyl Isocyanate with Allenes and Olefins[1-3]

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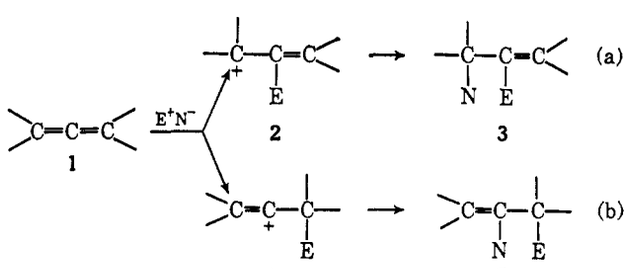
The addition of chlorosulfonyl isocyanate to allenes (2,4-dimethyl-2,3-pentadiene, 2-methyl-2,3-pentadiene, 2,3-pentadiene, 3-methyl-1,2-butadiene, pentamethyleneallene, 1,3-diphenylpropadiene, phenylpropadiene, and cyclononadiene) has been studied. In all cases, initial electrophilic attack occurred at the central carbon atom of the allenic system to produce, in the transition state, an allyl-type stabilized carbonium ion. Structures of the N-chlorosulfonyl-β-lactam cycloadducts and/or 2-carboxamido-1,3-butadiene products have been established on the basis of nmr spectroscopy and conversion into authentic derivatives prepared independently by the reaction of chlorosulfonyl isocyanate with the appropriate olefin. In the case of 3-methyl-1,2-butadiene, a third product identified by degradation and synthesis as 1-chlorosulfonyl-1-(2-carboxy-3-methyl-2-butenyl)urea was obtained. Chlorosulfonyl isocyanate added stereospecifically to *cis*- and *trans*-β-methylstyrene to lead to the *cis*- and *trans*-β-lactam, respectively, hydrolysis of which led to *erythro*- and *threo*-3-amino-2-methyl-3-phenylpropanoic acid hydrochloride. This experimentally determined relationship permitted assignment of the geometry of a number of β-lactam, carboxamido-1,3-butadiene, and amino acid products.

With a few exceptions, the principal mode of electrophilic (E^+) addition to cyclic and 1,3-disubstituted, straight-chain allenes has been *via* path a, while allene itself and monosubstituted allenes react predominantly *via* the vinyl carbonium (4) route (path b).[4] Attack by the nucleophile (N^-) on carbonium ions 2



and 4 complete the reaction to observed products 3 and 5, respectively.

Recently we reported that the stepwise 1,2-dipolar cycloaddition of chlorosulfonyl isocyante (CSI) to allenes [2,4-dimethyl-2,3-pentadiene (6a), 3-methyl-1,2-butadiene (6d), pentamethyleneallene (6e) and 1,2-cyclononadiene (6h)] proceeded *via* path a to produce initially, in the transition state, an allyl-type stabilized carbonium ion (7) leading ultimately to β-lactams (8, 9) and/or from the aqueous extract, 2-carboxamido-1,3-

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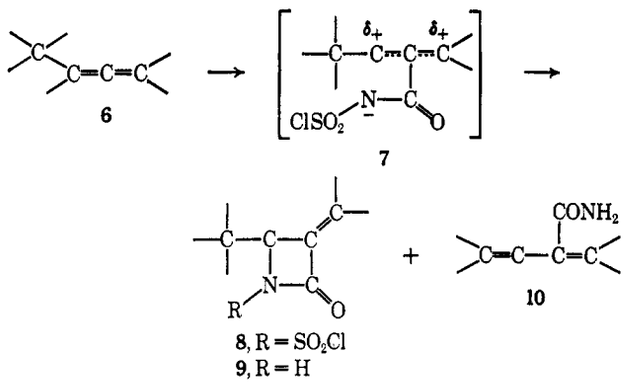
(2) Presented in part before the Organic Division, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstracts, p K76, and at the First International Congress of Heterocyclic Chemistry, the University of New Mexico, Albuquerque, N. M., June 12–15, 1967, Paper No. 76.

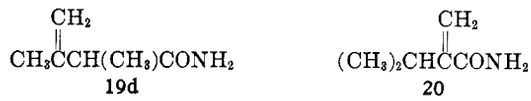
(3) Taken entirely from the Ph.D. Thesis of J. F. Kelly, 1969.

(4) For relevant references, including exceptions, *cf.* R. K. Sharma, B. A. Shoulders, and P. D. Gardner, *J. Org. Chem.*, **32**, 241 (1967); W. A. Waters and E. F. Kiefer, *J. Amer. Chem. Soc.*, **89**, 6261 (1968); and two recent reviews of allene chemistry: A. A. Petrov and A. V. Fedorova, *Russ. Chem. Rev.*, **33**, 1 (1964); H. Fischer in "Cumulenes," S. Patei, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 1060–1083.



butadienes (**10**).[5] The reaction between CSI and **6d** produced a third product (**11**) which seemed to be an adduct of 2 equiv of CSI with one of **6d**.[5] In this paper, we (i) report on CSI addition to allenes 2-methyl-2,3-pentadiene (**6b**), 2,3-pentadiene (**6c**), 1,3-diphenylpropadiene (**6f**), and phenylpropadiene (**6g**); (ii) provide experimental details of the reaction between CSI and **6a–h**, with proof of structure of both β-lactam and diene amide products; (iii) identify **11** by degradation and independent synthesis; (iv) provide experimental evidence for the stereospecific cycloaddition of CSI to *cis*- and *trans*-β-methylstyrene (*cis* and *trans* **16g**),[6] and (v) use this information to establish the geometry of a number of products.

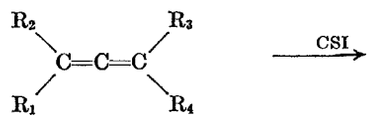
Addition of CSI to allenes **6a**, **b**, **d**, and **e** led to both N-chlorosulfonyl-β-lactams and dienes: respectively, 1-chlorosulfonyl-4,4-dimethyl-3-isopropylidene-2-azetidinone (**8a**, 67%) and 3-methyl-2-isopropylidene-3-butenamide (**10a**, 28%); 1-chlorosulfonyl-3-ethylidene-4,4-dimethyl-2-azetidinone (37%) (a 13:87 *cis* **8b**–*trans* **8b** mixture)[7] and 2-ethylidene-3-methyl-3-butenamide (25%) (a 29:71 *cis* **10b**–*trans* **10b** mixture);[7b] 1-chlorosulfonyl-3-methylene-4,4-dimethyl-2-azetidinone (**8d**, 23%), 3-methyl-2-methylene-3-butenamide (**10d**, 36%), and 1-chlorosulfonyl-1-(2-carboxy-3-methyl-2-butenyl)urea (**11**, 23%); and 1-chlorosulfonyl-3-methylene-1-azaspiro[3.5]nonan-2-one (**8e**, 40%) and 2-(1-cyclohexenyl)-2-propenamide (**10e**, 32%) (Chart I). Allene **6c** produced only diene 2-ethylidene-3-butenamide (**10c**, 31%), whereas **6f**, **g**, and **h** led only to N-chlorosulfonyl-β-lactams, 3-benzylidene-1-chlorosulfonyl-4-phenyl-2-azetidinone (**8f**, 63%), 1-chlorosulfonyl-3-methylene-4-phenyl-2-azetidinone (**8g**), and 10-chlorosulfonyl-10-azabicyclo[7.2.0]undec-1-ene-11-one (**8h**, 89%) (Chart I). No isolable products were obtained from the reaction of 1,2-heptadiene or 4-phenyl-1,2-butadiene with CSI. Cycloadduct **8g** was obtained in good yield as evidenced by the infrared spectrum, but polymerized within minutes *via* ring opening (since the carbonyl band at 5.5 μ shifted rapidly to *ca* 5.9 μ). Immediate benzenethiol–pyridine reduction of **8g** permitted the isolation of the stable β-lactam (**9g**) in 8% over-all yield. Similarly, reduction of **8a**, **b**, **d–f**, and **h** provided the unsubstituted β-lactams, **9a**, **b**, **d–f**, and **h**, respectively, in yields of 55–91%. In general, proof of β-lactam structures **9a**, **b**, and **d–h** was established by acid hydrolysis to unsaturated amino acid hydrochlorides **12a**, **b**, and **d–h**, which on hydrogenation led respectively, to **13a**, **b**, and **d–h**. Amino acid hydrochlorides **13a**, **b**, and **d–g** were independently prepared by the following sequence of reactions: (i) cycloaddition of CSI to 2,4-dimethyl-2-pentene (**16a**), 2-methyl-2-pentene (**16b**), 2-methyl-2-butene (**16d**), ethylidenecyclohexane (**16e**), *trans*-1,3-diphenylpropene (**16f**), and *cis*- and *trans*-β-methylstyrenes (*cis* **16g** and *trans* **16g**) led to the N-chlorosulfonyl-β-lactam products (**17a**, **b**, and **d–g**, respectively); (ii) reduction to β-lactams **18a**, **b**, and **d–g**, respectively; and (iii) acid hydrolysis to **13a**, **b**, and **d–g**. Proof of structure of diene amides **10a–e** was achieved by reduction to the following saturated derivatives: diisopropylacetamide (**15a**),[8] 2-isopropylbutanamide (**15b**),[9] 2-ethylbutanamide (**15c**),[10] 2,3-dimethylbutanamide (**15d**),[5,11] and 2-cyclohexylpropanamide (**15e**),[12] respectively. In the case of **10d**, hydrogenation over Pd–C gave an 85% yield of partially reduced 2,3-dimethyl-2-butenamide (**14d**) and 15% of **15d**. We must revise our earlier suggestion[13] and now conclude that the conversion **10d** → **14d** must involve 1,4 reduction since neither of the independently prepared "1,2-reduction" products 2-methyl-3-methylenebutanamide (**19d**) and 3-methyl-2-methylenebutanamide (**20**) isomerize to **14d** under the catalytic conditions (5% Pd–C) employed. Finally, minor products (4–8%) of the addition of CSI to **16a**, **b**, and **d** included 3-methyl-2-isopropyl-3-butenamide (**19a**), 2-ethyl-3-methyl-3-butenamide (**19b**), and **19d**, respectively. Hydrogenation of **19a** and **b** led to quantitative conversion into **15a** and **b**, respectively, as did **14d**, **19d**, and **20** into **15d**.



Structure of 11 (Chart II).—The identity of **11** was established as 1-chlorosulfonyl-1-(2-carboxy-3-methyl-2-butenyl)urea by benzenethiol–pyridine reduction to 1-(2-carboxy-3-methyl-2-butenyl)urea (**22**). Both the ozonation of **11** and permanganate–periodate oxidation of **22** produced acetone, isolated as the 2,4-DNP derivative, thus suggesting the same isopropylidene moiety in each. Catalytic reduction of **22** led to 1-(2-carboxy-3-methylbutyl)urea (**23**), alkaline hydrolysis of which gave 2-carboxy-3-methylbutylamine (**24**). Benzoylation of **24** under Schotten–Bauman conditions led to crystalline 1-benzamido-2-carboxy-3-methylbutane (**25**). A parallel sequence of reactions on **22** → **26** → **27** with a final catalytic reduction also led to **25**. Although **23** and **24** were isolated, purified, and characterized, the reaction sequence **22** → **23** → **24** → **25** could be accomplished in 47% over-all yield without isolation of intermediates. Authentic **25** was prepared from diethyl isopropylmalonate (**28**) *via* the half-ester (**29**), followed by a Mannich reaction to ethyl 3-methyl-2-methylenebutanoate (**30**) and its hydrolysis to **31**. A Michael addition of HBr to **31** led to 2-bromomethyl-3-

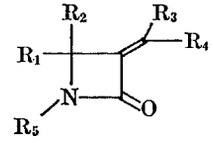
(5) E. J. Moriconi and J. F. Kelly, *J. Amer. Chem. Soc.*, **88**, 3657 (1966).
(6) E. J. Moriconi and J. F. Kelly, *Tetrahedron Lett.*, 1435 (1968).
(7) (a) Based on nmr analysis of the unsubstituted β-lactam product mixture *cis* **9b** and *trans* **9b**; (b) the *cis* or *trans* designation refers to the position of the olefinic methyl group *cis* or *trans* to the adjacent C=O group.
(8) F. C. B. Marshall, *J. Chem. Soc.*, 2754 (1930).
(9) G. S. Slomp, Jr., and J. L. Johnson, *J. Amer. Chem. Soc.*, **80**, 915 (1958).
(10) H. Koch and F. Hillberath, *Ber.*, **73**, 1171 (1940).
(11) C. D. Nenitzescu and I. Chicos, *ibid.*, **68**, 1584 (1935).
(12) R. S. Thakur, *J. Chem. Soc.*, 1481 (1933).
(13) Reference 5, footnote 11.

CHART I



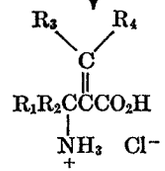
6a, $R_1 = R_2 = R_3 = R_4 = CH_3$
b, $R_1 = R_2 = R_3 = CH_3$; $R_4 = H$
c, $R_1 = R_4 = H$; $R_2 = R_3 = CH_3$
d, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
e, $R_1R_2 = -(CH_2)_5-$; $R_3 = R_4 = H$
f, $R_1 = R_3 = H$; $R_2 = R_4 = C_6H_5$
g, $R_1 = R_3 = R_4 = H$; $R_2 = C_6H_5$
h, $R_2R_3 = -(CH_2)_6-$; $R_1 = R_4 = H$

CSI



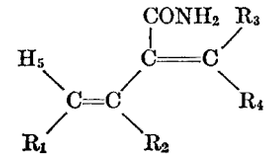
8a, $R_1 = R_2 = R_3 = R_4 = CH_3$; $R_5 = SO_2Cl$
9a, $R_1 = R_2 = R_3 = R_4 = CH_3$; $R_5 = H$
cis **8b**,[7b] $R_1 = R_2 = R_4 = CH_3$; $R_3 = H$; $R_5 = SO_2Cl$
trans **8b**,[7b] $R_1 = R_2 = R_3 = CH_3$; $R_4 = H$; $R_5 = SO_2Cl$
cis **9b**,[7b] $R_1 = R_2 = R_4 = CH_3$; $R_3 = R_5 = H$
trans **9b**,[7b] $R_1 = R_2 = R_3 = CH_3$; $R_4 = R_5 = H$
8d, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$; $R_5 = SO_2Cl$
9d, $R_1 = R_2 = CH_3$; $R_3 = R_4 = R_5 = H$
8e, $R_1R_2 = -(CH_2)_5-$; $R_3 = R_4 = H$; $R_5 = SO_2Cl$
9e, $R_1R_2 = -(CH_2)_5-$; $R_3 = R_4 = R_5 = H$
8f, $R_1 = R_4 = H$; $R_2 = R_3 = C_6H_5$; $R_5 = SO_2Cl$
9f, $R_1 = R_4 = R_5 = H$; $R_2 = R_3 = C_6H_5$
8g, $R_1 = R_3 = R_4 = H$; $R_2 = C_6H_5$; $R_5 = SO_2Cl$
9g, $R_1 = R_3 = R_4 = R_5 = H$; $R_2 = C_6H_5$
8h, $R_2R_3 = -(CH_2)_6-$; $R_1 = R_4 = H$; $R_5 = SO_2Cl$
9h, $R_2R_3 = -(CH_2)_6-$; $R_1 = R_4 = R_5 = H$

HCl



12a, $R_1 = R_2 = R_3 = R_4 = CH_3$
b, $R_1 = R_2 = R_3 = CH_3$; $R_4 = H$
d, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
e, $R_1R_2 = -(CH_2)_5-$; $R_3 = R_4 = H$
f, $R_1 = R_3 = H$; $R_2 = R_4 = C_6H_5$
g, $R_1 = R_3 = R_4 = H$; $R_2 = C_6H_5$
h, $R_2R_3 = -(CH_2)_6-$; $R_1 = R_4 = H$

+



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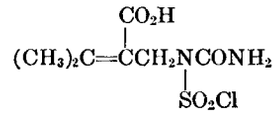
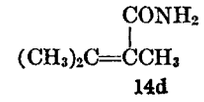


11

10a, $R_1 = H$; $R_2 = R_3 = R_4 = CH_3$
cis **b**, $R_1 = R_3 = H$; $R_2 = R_4 = CH_3$
trans **b**, $R_1 = R_4 = H$; $R_2 = R_3 = CH_3$
c, $R_1 = R_2 = R_3 = H$; $R_4 = CH_3$
d, $R_1 = R_3 = R_4 = H$; $R_2 = CH_3$
e, $R_1R_2 = -(CH_2)_4-$; $R_3 = R_4 = H$

[H], Pd–C



14d

[H], PtO_2

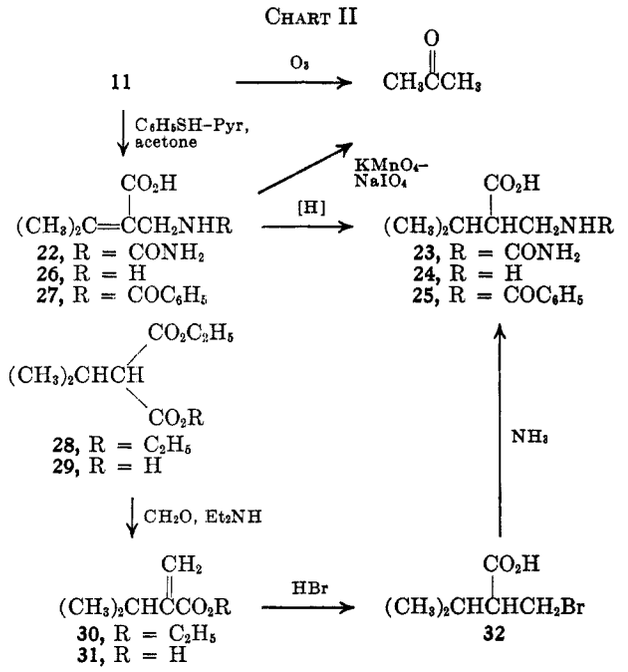
[H]

$R_1R_2CHCONH_2$

15a, $R_1 = R_2 = CH(CH_3)_2$
b, $R_1 = CH(CH_3)_2$; $R_2 = C_2H_5$
c, $R_1 = R_2 = C_2H_5$
d, $R_1 = CH(CH_3)_2$; $R_2 = CH_3$
e, R_1 = cyclohexyl; $R_2 = CH_3$

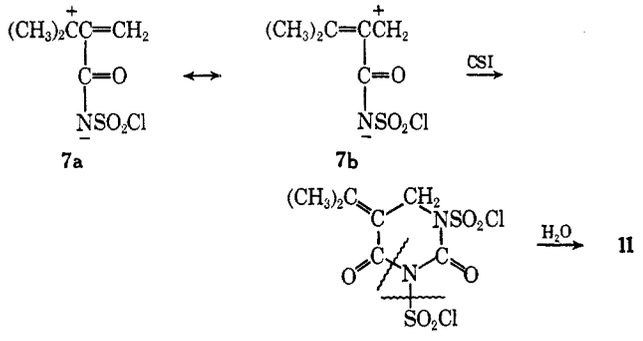
[H]
[H]
CSI
HCl
+
13a, R1 = R2 = CH3; R3 = CH(CH3)2
b, R1 = R2 = CH3; R3 = C2H5
d, R1 = R2 = R3 = CH3
e, R1R2 = -(CH2)5-; R3 = CH3
erythro f, R1 = H; R2 = C6H5; R3 = CH2C6H5
threo f, R1 = C6H5; R2 = H; R3 = CH2C6H5
erythro g, R1 = H; R2 = C6H5; R3 = CH3
threo g, R1 = C6H5; R2 = H; R3 = CH3
h, R1 = H; R2R3 = -(CH2)4-
meso i, R1 = H; R2 = R3 = C2H5
dl i, R1 = R3 = C2H5; R2 = H
19a, R1 = H; R2 = CH3; R3 = CH(CH3)2
b, R1 = H; R2 = CH3; R3 = C2H5
d, R1 = H; R2 = R3 = CH3
i, R1 = CH3; R2 = H; R3 = C2H5
16a, R1 = R2 = CH3; R3 = H; R4 = CH(CH3)2
b, R1 = R2 = CH3; R3 = H; R4 = C2H5
d, R1 = R2 = R3 = CH3; R4 = H
e, R1R2 = -(CH2)5-; R3 = H; R4 = CH3
trans f, R1 = R3 = H; R2 = C6H5; R4 = CH2C6H5
cis g, R1 = R4 = H; R2 = C6H5; R3 = CH3
trans g, R1 = R3 = H; R2 = C6H5; R4 = CH3
cis i, R1 = R4 = H; R2 = R3 = C2H5
trans i, R1 = R3 = H; R2 = R4 = C2H5
17a, R1 = R2 = CH3; R3 = H; R4 = CH(CH3)2; R5 = SO2Cl
18a, R1 = R2 = CH3; R3 = R5 = H; R4 = CH(CH3)2
17b, R1 = R2 = CH3; R3 = H; R4 = C2H5; R5 = SO2Cl
18b, R1 = R2 = CH3; R3 = R5 = H; R4 = C2H5
17d, R1 = R2 = R3 = CH3; R4 = H; R5 = SO2Cl
18d, R1 = R2 = R3 = CH3; R4 = R5 = H
17e, R1R2 = -(CH2)5-; R3 = H; R4 = CH3; R5 = SO2Cl
18e, R1R2 = -(CH2)5-; R3 = R5 = H; R4 = CH3
trans 17f, R1 = R3 = H; R2 = C6H5; R4 = CH2C6H5; R5 = SO2Cl
cis 18f, R1 = R4 = R5 = H; R2 = C6H5; R3 = CH2C6H5
trans 18f, R1 = R3 = R5 = H; R2 = C6H5; R4 = CH2C6H5
cis 17g, R1 = R4 = H; R2 = C6H5; R3 = CH3; R5 = SO2Cl
trans 17g, R1 = R3 = H; R2 = C6H5; R4 = CH3; R5 = SO2Cl
cis 18g, R1 = R4 = R5 = H; R2 = C6H5; R3 = CH3
trans 18g, R1 = R3 = R5 = H; R2 = C6H5; R4 = CH3
cis 17i, R1 = R4 = H; R2 = R3 = C2H5; R5 = SO2Cl
trans 17i, R1 = R3 = H; R2 = R4 = C2H5; R5 = SO2Cl
cis 18i, R1 = R4 = R5 = H; R2 = R3 = C2H5
trans 18i, R1 = R3 = R5 = H; R2 = R4 = C2H5

CHART II



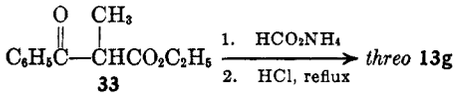
methylbutanoic acid (**32**), treatment of which with aqueous ammonia led to the primary amine **24** and ultimately **25**.

The mechanism of formation of **11** is consistent with the initial formation of the allyl carbonium ion **7** (path a), followed successively by the 1,4-dipolar cycloaddition of **7b** to a second molecule of the electrophilic dipolarophile CSI and hydrolytic cleavage to **11**.[14]

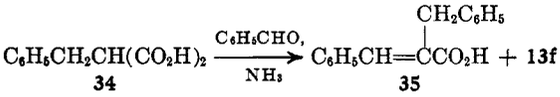


Product Geometry.—We recently reported the stereospecific *cis* addition of CSI to *cis*- (*cis* **16g**) and *trans*-β-methylstyrene (*trans* **16g**) to yield 2 + 2 cycloadducts, N-chlorosulfonyl-*cis*- (*cis* **17g**) and -*trans*-3-methyl-4-phenyl-2-azetidinone (*trans* **17g**).[6] The retention of configuration of R_1–R_4 in *cis* and *trans* **17g** is unequivocally supported by nmr data. Thus the eclipsed *cis* protons in *cis* **17g** show the expected vicinal coupling of 7.25 Hz while the *trans*-skewed protons in *trans* **17g** displayed vicinal coupling of 4.00 Hz. Furthermore, the methyl protons (R_3) in *cis* **17g** are in the shielding region of the *cis*-phenyl ring (R_2) and appear as a doublet upfield (0.54 ppm) relative to the *trans*-methyl protons (R_4) in *trans* **17g**.[15,16]

Benzenethiol–pyridine reduction of *cis* and *trans* **17g**, respectively, led to *cis* and *trans* **18g**; acid hydrolysis quantitatively converted the *cis*-β-lactam into *erythro*-3-amino-2-methyl-3-phenylpropanoic acid hydrochloride (*erythro* **13g**), whereas the *trans*-β-lactam led to the *threo* isomer (*threo* **13g**). This experimentally established relationship (*cis*-β-lactam → *erythro*-amino acid and *trans*-β-lactam → *threo*-amino acid) permitted the identification and assignment of the geometry of a number of products. (i) The reduced, acid hydrolysis product of **9g** was spectroscopically determined to consist of a 63:37 mixture of *erythro* **13g** and *threo* **13g**. (ii) Leuckart reduction of ethyl 2-benzoylpropanoate (**33**) led to an 18% yield of **13g** identified as *threo* **13g**.



(iii) The reaction sequence commencing with allene **6f** → **8f** → **9f** → **18f** led solely to the *cis* isomer of 3-benzyl-4-phenyl-2-azetidinone (*cis* **18f**) since acid hydrolysis of *cis* **18f** quantitatively converted it into *erythro*-3-amino-2-benzyl-3-phenylpropanoic acid hydrochloride (*erythro* **13f**). The alternative route to this amino acid (*via* **9f** → **12f** → **13f**) also produced only *erythro* **13f**. The homogeneity of *cis* **18f** further suggested that the olefinic phenyl substituent (R_3) in the N-chlorosulfonyl-β-lactam precursor **8f** is *trans* to the carbonyl group.[7b] (iv) The reaction sequence commencing with the olefin *trans* **16f** → **17f** → **18f** led solely to the *trans* isomer of 3-benzyl-4-phenyl-2-azetidinone (*trans* **18f**) since acid hydrolysis quantitatively converted it into *threo*-3-amino-2-benzyl-3-phenylpropanoic acid hydrochloride (*threo* **13f**). (v) Finally, a Mannich reaction on benzylmalonic acid (**34**) led to 2-benzylcinnamic acid (**35**, 19%) and an 18% yield of a 58:42 *erythro*–*threo* mixture of **13f**. Earlier in this



paper, we had noted that the addition of CSI to 2-methyl-2,3-pentadiene (**6b**) had led to *cis*–*trans* isomers of both **8b** and **10b** in which the less sterically hindered *trans* isomer predominated.[7b] These conclusions were based on an nmr analysis of **9b** (reduction product of **8b**) and **10b**. Thus, in both *cis* **9b** and *cis* **10b**, the olefinic methyl group is in the plane of and proximate to the adjacent C=O group, and appears downfield (0.21 and 0.44 ppm, respectively) in the nmr spectrum, relative to the same substituent in *trans* **9b** and *trans* **10b**.

(14) At the First International Congress of Heterocyclic Chemistry,[2] R. Huisgen reported on "1,4-Dipolar Cycloaddition. A General Principle of Heterocyclic Syntheses." The formation of **11** is a specific example of this synthetic principle. A related example has recently been reported [H. Ulrich, B. Tucker, and A. A. R. Sayigh, *J. Amer. Chem. Soc.*, **90**, 528 (1968)].

(15) K. D. Barrow and T. M. Spotswood, *Tetrahedron Lett.*, 3326 (1965).

(16) Similar stereospecificity was observed in the cycloaddition of CSI to *cis*- (*cis* **16i**) and *trans*-3-hexene (*trans* **16i**). Analytical and spectral data, and results of decoupling experiments for *cis* and *trans* **17g**, and *cis* and *trans* **17i** are summarized in the Experimental Section.

Experimental Section[17-22]

Reaction of CSI with Allenes (16).—The general procedure used was as follows. A solution of the allene in anhydrous ether (15 ml/0.1 mol) was added dropwise to an ice bath cooled, stirred solution of an equimolar amount of CSI in the same solvent (20 ml/0.1 mol). The solution was stirred until the ir spectrum showed the absence of the allene and isocyanate peaks (*ca.* 5.1 and 4.4 μ, respectively) (15 min to 3 hr) and poured onto 10–20 g of ice. The ether layer was extracted with eight 15-ml portions of water and the aqueous extracts were combined with the water layer. The ether moiety was dried (Na_2SO_4) and evaporated to dryness under a N_2 stream. The residue was extracted or dissolved in boiling solvent; the solution was decolorized (charcoal) and cooled to −20° to give the N-chlorosulfonyl-β-lactam product (**8**). Concentration of the filtrate occasionally gave additional amounts of product.

The combined aqueous extracts were extracted for 4–5 days (Raab extractor) with CH_2Cl_2. The methylene chloride solution after work-up led to the unsaturated amide product (**10**).

Variations in isolation procedure for **8** and **10** are noted under each allene.

2,4-Dimethyl-2,3-pentadiene (6a) (10.0 g, 0.10 mol) gave 16.3 g (67%) of **1-chlorosulfonyl-4,4-dimethyl-3-isopropylidene-2-azetidinone (8a)**: mp 71–72° (from hexane); uv max (CH_3OH), 241 mμ (ε 22,000); ir (KBr), 5.58 μ (C=O).

Anal. Calcd for $C_8H_{12}NO_3SCl$: C, 40.45; H, 5.09; N, 5.89. Found: C, 40.55; H, 5.13; N, 6.20.

Evaporation of the CH_2Cl_2 extract led to crude **3-methyl-2-isopropylidene-3-butenamide (10a)** which was dissolved in 50 ml of ether and decolorized (charcoal), and 50 ml of hexane was added. The solution was boiled until the temperature reached 50° and then cooled to give 4.0 g (29%) of pure **10a** as needles: mp 134–135° dec and sublimes; ir (KBr), 6.09 μ (C=O).

Anal. Calcd for $C_8H_{13}NO$: C, 69.04; H, 9.41; N, 10.01. Found: C, 68.88; H, 9.37; N, 10.11.

2-Methyl-2,3-pentadiene (6b) (8.2 g, 0.1 mol) gave 8.3 g (37%) of **1-chlorosulfonyl-3-ethylidene-4,4-dimethyl-2-azetidinone (8b)** after extraction with five 30-ml portions of boiling pentane: mp 92–93° (from pentane); uv max (CH_3OH), 229 mμ (ε 23,500); ir (KBr), 5.58 μ (C=O).

Anal. Calcd for $C_7H_{10}NO_3SCl$: C, 37.59; H, 4.51; N, 6.26. Found: C, 37.72; H, 4.73; N, 6.10.

The methylene chloride extract was evaporated to 25 ml *in vacuo* and poured slowly into 150 ml of boiling hexane. The boiling was continued until the CH_2Cl_2 had evaporated. The hexane was decanted and the residual oil was further extracted with three 25-ml portions of boiling hexane. The hexane extracts were combined and were evaporated to 100 ml, cooled, and filtered to give 3.2 g (25%) of a 29% *cis*–71% *trans* mixture of **2-ethylidene-3-methyl-3-butenamide (10b)**: mp 55–57°; uv max (CH_3OH), 227 mμ (ε 23,100); ir (KBr), 6.08 μ (C=O); nmr ($CDCl_3$), for *cis* **10b**, δ 6.40 (broad singlet, 2, NH_2), 5.67 (q, 1, J = 7 Hz, $=CHCH_3$), 5.05 and 4.85 (two broad singlets, 2, $=CH_2$), 1.84 (s, 3, CH_3), and 1.78 (doublet with one peak under methyl singlet, 3, $=CHCH_3$); for *trans* **10b**, δ 7.20 (broad singlet, 2, NH_2), 6.65 (q, 1, J = 7 Hz, $=CHCH_3$), 5.23 and 4.95 (two broad singlets, 2, $=CH_2$), 1.84 (s, 3, CH_3), and 1.71 (d, 3, J = 7 Hz, $=CHCH_3$).

Anal. Calcd for $C_7H_{11}NO$: C, 67.17; H, 8.86; N, 11.19. Found: C, 66.81; H, 9.13; N, 10.81.

2,3-Pentadiene (6c) (4.2 g, 0.062 mol) gave 2.1 g (31%) of **3-carboxamido-1,3-pentadiene (10c)**. After extraction of the ether layer with water, the combined aqueous extracts were then extracted with methylene chloride (Raab extractor) for 5 days. The methylene chloride extract was evaporated to dryness, and the residue was extracted with three 20-ml portions of boiling hexane to give, on cooling, **10c**: mp 100–102°; uv max (CH_3OH), 220 mμ (ε 20,200); ir (KBr), 6.08 μ (C=O).

Anal. Calcd for C_6H_9NO: C, 64.85; H, 8.15; N, 12.60. Found: C, 64.52; H, 8.19; N, 12.35.

3-Methyl-1,2-butadiene (6d) (5.0 g, 0.074 mol) gave 3.5 g (23%) of **1-chlorosulfonyl-4,4-dimethyl-3-methylene-2-azetidinone (8d)** after extraction with three 30-ml portions of boiling pentane: mp 51–52° (from pentane); uv max (CH_3OH), 218 mμ (ε 10,000); ir (KBr), 5.52 μ (C=O).

Anal. Calcd for $C_6H_8NO_3SCl$: C, 34.37; H, 3.85; N, 6.68. Found: C, 34.51; H, 4.03; N, 6.80.

After the boiling pentane extraction, the yellow, semisolid residue was extracted with three 30-ml portions of boiling ether. Hexane was added to the hot combined ether extracts to the cloud point. The solution was boiled again, decolorized (charcoal), and filtered. Additional hexane was added (total *ca.* 50 ml), and the solution was boiled until **1-chlorosulfonyl-1-(2-carboxy-3-methyl-2-butenyl)urea (11)** began to precipitate. After cooling, **11** was filtered. Further concentration of the filtrate led to additional **11**: total yield 2.3 g (23%) (from ether–hexane); mp 126–127°; uv max (CH_3OH), 215 mμ (ε 12,000); ir (KBr), 5.95 and 6.13 μ (C=O).

Anal. Calcd for $C_7H_{11}N_2O_5SCl$: C, 31.06; H, 4.10; N, 10.35; mol wt, 271. Found: C, 31.66; H, 4.38; N, 10.36; mol wt (isothermal distillation), 288.

The methylene chloride extract was evaporated to dryness and the residue was recrystallized from ether–hexane to give 2.9 g (36%) of **3-methyl-2-methylene-3-butenamide (10d)**, mp 70° (with polymerization). Amide **10d** polymerizes on standing in the solid state within 1 day, but it is stable for several days in ether solution: uv max (CH_3OH), 223 mμ (ε 7800); ir (KBr), 6.09 μ (C=O).

Anal. Calcd for C_6H_9NO: C, 64.85; H, 8.15; N, 12.60. Found: C, 64.93; H, 8.24; N, 12.32.

Pentamethyleneallene (6e) (10.0 g, 0.09 mol) gave 9.15 g (40%) of **1-chlorosulfonyl-3-methylene-1-azaspiro[3.5]nonan-2-one (8e)**: mp 96–97° (from hexane); uv max (CH_3OH), 215 mμ (ε 2200); ir (KBr), 5.56 μ (C=O).

Anal. Calcd for $C_9H_{12}NO_3SCl$: C, 43.28; H, 4.85; N, 5.61. Found: C, 43.44; H, 5.02; N, 5.86.

The methylene chloride extract was evaporated *in vacuo* to dryness, and the residue was recrystallized from ether–hexane to give 2.4 g (32%) of **2-(1-cyclohexenyl)-2-propenamide (10e)**: mp 135–137°; uv max (CH_3OH), 234 mμ (ε 8,500); ir (KBr), 6.05 μ (C=O).

Anal. Calcd for $C_9H_{13}NO$: C, 71.48; H, 8.66; N, 9.27. Found: C, 71.78; H, 8.76; N, 9.38.

1,3-Diphenylpropadiene (6f) (2.0 g, 0.01 mol) gave 2.2 g (63%) of **3-benzylidene-1-chlorosulfonyl-4-phenyl-2-azetidinone (8f)**. After addition of **6f** to CSI, the mixture was stirred for 1 hr at room temperature, after which it was poured into 50 ml of hexane. Crude **8f** was filtered and recrystallized from ether–hexane to give **8f** as needles: mp 98–99°; uv max (CH_3OH), 219 mμ (ε 6100) and 304 (13,000); ir (KBr), 5.58 μ (C=O).

Anal. Calcd for $C_{16}H_{12}NO_3SCl$: C, 57.57; H, 3.62; N, 4.20. Found: C, 57.31; H, 3.64; N, 4.24.

Phenylpropadiene (6g) (6.4 g, 0.06 mol) gave 0.62 g (8%) of **3-methylene-4-phenyl-2-azetidinone (9g)**. After addition of **6g** to CSI, the mixture was stirred for 2 hr and cooled to −40°; 10.5 g (0.095 mol) of thiophenol was added quickly, followed by slower addition (30 min) of 4.5 g (0.055 mol) of pyridine. The mixture was stirred for an additional hr at −40°, after which 75 ml of ethanol were added. The solution was evaporated *in vacuo* to a volume of 50 ml and then cooled to −20°. The precipitated diphenyl disulfide was filtered, and the filtrate was evaporated

(17) Melting points are corrected; boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer 337 grating spectrophotometer; ultraviolet spectra were recorded on a Cary 15 spectrophotometer. Nmr spectra were obtained on a Varian Associates A-60A spectrometer using TMS as an internal standard in organic solvents and the DOH peak (δ 4.67) in D_2O solutions. Double resonance experiments on *cis* and *trans* **17g** and *cis* and *trans* **17i** (Table I) were conducted with a Varian Associates 6058A spin decoupler. Full nmr data are available in ref 3. Gas chromatograms were run on a Perkin-Elmer 880 instrument with a flame ionization detector and using a column packed with 10% SE 30 on Chromosorb W. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. CSI was obtained from American Hoechst Corp. **2-Methyl-2,3-pentadiene (6b)**, **2,3-pentadiene (6c)**, and **phenylpropadiene (6g)** were prepared from the appropriate olefin using Skattebøl's general two-step procedure;[18] **3-methyl-1,2-butadiene (6d)** and **pentamethylene allene (6e)** were synthesized by reduction of 3-chloro-3-methyl-1-butyne and 1-ethnyl-1-chlorocyclohexane, respectively, using lithium aluminum hydride in tetrahydrofuran;[19] **1,2-cyclononadiene (6h)** was prepared in the one-step procedure from cyclooctene.[20] **1,3-Diphenylpropadiene (6f)** was synthesized *via* prototropic rearrangement of 1,3-diphenylpropyne by adsorption on a basic alumina column;[21] *trans*-**1,3-diphenylpropene (16f)** was prepared by the Bamford–Stevens procedure.[22] **2,4-Dimethyl-2,3-pentadiene (6a)** and all other olefins (**16a–e, g,** and **i**) were obtained from the Chemical Samples Co.

(18) L. Skattebøl, *Acta Chem. Scand.*, **17**, 1683 (1963).

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

(20) K. G. Untch, D. J. Martin, and N. T. Castellucci, *ibid.*, **30**, 3572 (1965).

(21) T. L. Jacobs and D. Danker, *ibid.*, **22**, 1424 (1957).

(22) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

in vacuo. The residual oil was dissolved in the minimal amount of ether, deposited on a 2 × 25 cm column (Woelm neutral alumina, activity grade I), and eluted successively with equal volumes (200 ml) of hexane, CCl_4, and $CHCl_3$. Crude **9** appeared in the CCl_4 fraction, and after evaporation of the solvent, was recrystallized twice from hexane to give pure **9g**: mp 106–107°; ir (KBr), 5.75 and 5.84 μ (C=O).

Anal. Calcd for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.58; H, 5.68; N, 8.88.

1,2-Cyclononadiene (6h) (2.5 g, 0.02 mol) gave 4.7 g (89%) of **10-chlorosulfonyl-10-azabicyclo[7.2.0]undec-1-en-11-one (8h)** after extraction with three 20-ml portions of boiling pentane. Recrystallization several times by cooling in Dry Ice–acetone bath, filtering, redissolution in pentane, and cooling to Dry Ice–acetone temperature gave pure **8h**: mp 45–46°; uv max (CH_3OH), 234 mμ (ε 14,500); ir (KBr), 5.51 μ (C=O).

Anal. Calcd for $C_{10}H_{14}NO_3SCl$: C, 45.54; H, 5.35; N, 5.31. Found: C, 45.47; H, 5.47; N, 5.09.

Benzenethiol–Pyridine Reduction of N-Chlorosulfonyl-β-Lactams (8) to β-Lactams 9.—The general procedure used was as follows. A solution of pyridine (20% mol excess) in acetone (15 ml/0.1 mol) was added dropwise (30 min) to a stirred solution of **8** and benzenethiol (2 equiv) in acetone (25 ml/0.1 mol), maintained at −30°. After stirring for an additional 30 min, an amount of water, equal to the volume of solvent acetone, was added slowly with stirring. The precipitated diphenyl disulfide was filtered, and the filtrate was extracted with six 25-ml portions of ether. The combined ether extracts were dried (Na_2SO_4) and evaporated to dryness, and the residue was recrystallized to give **9**. Any variations in isolation procedures for **9** are noted under each β-lactam.

Compound **8a** (11.9 g, 0.05 mol) gave 7.0 g (77%) of **4,4-dimethyl-3-isopropylidene-2-azetidinone (9a)**: mp 99–100° (from hexane); uv max (CH_3OH), 217 mμ (ε 16,900); ir (KBr), 5.78 and 5.85 μ (C=O).

Anal. Calcd for $C_8H_{13}NO$: C, 69.04; H, 9.41; N, 10.01. Found: C, 68.78; H, 9.58; N, 9.82.

The *cis–trans* **8b** mixture (4.5 g, 0.03 mol) gave 2.4 g (64%) of a 13% *cis*–87% *trans* mixture of **3-ethylidene-4,4-dimethyl-2-azetidinone (9b)**: mp 56–57° (needles from hexane); ir (KBr), 5.71 μ (C=O); nmr ($CDCl_3$), for *trans* **9b**, δ 7.65 (broad singlet, 1, NH), 6.03 (q, 1, J = 7 Hz, =CH), 1.73 (d, 3, J = 7 Hz, $=CHCH_3$), and 1.47 (s, 6, CH_3), for *cis* **9b**, δ 7.65 (broad singlet, 1, NH), 5.61 (q, 1, J = 7 Hz, =CH), 1.94 (d, 3, J = 7 Hz, $=CHCH_3$), and 1.38 (s, 6, CH_3).

Anal. Calcd for $C_7H_{11}NO$: C, 67.17; H, 8.86; N, 11.19. Found: C, 67.33; H, 8.81; N, 11.47.

Compound **8d** (10 g, 0.125 mol) gave 6.15 g (55%) of **3-methylene-4,4-dimethyl-2-azetidinone (9d)**. After evaporation of the ether extracts to dryness, the residual yellow oil was extracted with six 40-ml portions of boiling pentane. On cooling, **9d** crystallized as long needles. Sublimation (50°, 1 mm) led to analytically pure **9d**: mp 64–65°; uv max (CH_3OH) 229 mμ (ε 2900); ir (CS_2), 5.63 and 5.69 μ (C=O); Raman ($CHCl_3$), 3.24 (=CH_2), 5.80 (monomer C=C), and 5.89 μ (dimer–polymer C=C).

Anal. Calcd for C_6H_9NO: C, 64.83; H, 8.17; N, 12.60. Found: C, 65.15; H, 8.42; N, 12.59.

Compound **8e** (11.1 g, 0.045 mol) gave 4.5 g (68%) of **3-methylene-1-azaspiro[3.5]nonan-2-one (9e)**: mp 114–115° (needles from hexane); uv max (CH_3OH), 227 mμ (ε 2300); ir (KBr), 5.73 and 5.83 μ (C=O).

Anal. Calcd for $C_9H_{13}NO$: C, 71.48; H, 8.66; N, 9.27. Found: C, 71.76; H, 8.69; N, 9.50.

Compound **8f** (2.0 g, 0.006 mol) gave 1.25 g (91%) of **3-benzylidene-4-phenyl-2-azetidinone (9f)**. After addition of water, the solid which precipitated contained both diphenyl disulfide and **9f**. This solid material was filtered and washed successively with three 30-ml portions of H_2O and five 30-ml portions of cold hexane. The residual crude β-lactam was recrystallized from acetone: mp 219–221°; uv max (CH_3OH), 222 mμ (ε 9000) and 272 (10,700); ir (KBr), 5.77 and 5.88 μ (C=O).

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.97; H, 5.54; N, 6.16.

Compound **8h** (3.0 g, 0.011 mol) gave 1.15 g (40%) of **10-azabicyclo[7.2.0]undec-1-en-11-one (9h)**: mp 144–145° (from hexane); uv max (CH_3OH), 212 mμ (ε 11,400); ir (KBr), 5.71 and 5.81 μ (C=O).

Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.70; H, 9.24; N, 8.60.

Concentrated Hydrochloric Acid Hydrolysis of β-Lactams 9 to Amino Acid Hydrochlorides (12).—The general procedure used was as follows. Concentrated HCl (2 ml/g) was added to analytically pure **9** and stirred for 30 min. The excess H_2O and HCl was removed *in vacuo* to give a quantitative yield of pure **12**. In the specific cases noted, heating was required to effect hydrolysis and/or an acetone wash was used.

Compound **9a** gave **3-amino-3-methyl-2-isopropylidenebutanoic acid hydrochloride (12a)**: mp 215° dec; ir (KBr), 5.84 μ (C=O).

Anal. Calcd for $C_8H_{16}NO_2Cl$: C, 49.61; H, 8.33; N, 7.23. Found: C, 49.38; H, 8.24; N, 7.34.

Compound **9b** gave **3-amino-2-ethylidene-3-methylbutanoic acid hydrochloride (12b)**: mp 213° dec; ir (KBr), 5.97 μ (C=O).

Anal. Calcd for $C_7H_{14}NO_2Cl$: C, 46.80; H, 7.86; N, 7.79. Found: C, 46.59; H, 7.80; N, 7.55.

Compound **9d** gave **3-amino-2-methylene-3-methylbutanoic acid hydrochloride (12d)**: mp 168° dec; ir (KBr), 5.89 μ (C=O).

Anal. Calcd for $C_6H_{12}NO_2Cl$: C, 43.52; H, 7.30; N, 8.46. Found: C, 43.60; H, 7.29; N, 8.69.

Compound **9e** gave **2-(1-aminocyclohexyl)-2-propenoic acid hydrochloride (12e)** after washing with cold acetone: mp 211° dec; ir (KBr), 5.90 μ (C=O).

Anal. Calcd for $C_9H_{16}NO_2Cl$: C, 52.55; H, 7.84; N, 6.81. Found: C, 52.78; H, 8.09; N, 6.64.

Compound **9f** was heated at 80° in concentrated HCl for 30 min to give **3-amino-2-benzylidene-3-phenylpropanoic acid hydrochloride (12f)**. The residue was treated with 25 ml of boiling acetone and filtered: mp 251–252° dec; uv max (CH_3OH), 257 mμ (ε 18,600); ir (KBr), 5.92 μ (C=O).

Anal. Calcd for $C_{16}H_{16}NO_2Cl$: C, 66.32; H, 5.57; N, 4.83. Found: C, 66.15; H, 5.63; N, 5.16.

Compound **9g** gave **3-amino-2-methylene-3-phenylpropanoic acid hydrochloride (12g)** after washing with cold acetone: mp 197° dec; ir (KBr), 5.78 μ (C=O).

Anal. Calcd for $C_{10}H_{12}NO_2Cl$: C, 56.23; H, 5.66; N, 6.56. Found: C, 56.22; H, 5.64; N, 6.26.

Compound **9h** gave **3-amino-2-carboxy-1-cyclononene hydrochloride (12h)**: mp 145–146° dec; uv max (CH_3OH), 212 mμ (ε 12,500); ir (KBr), 5.81 μ (C=O).

Anal. Calcd for $C_{10}H_{18}NO_2Cl$: C, 54.67; H, 8.26; N, 6.38. Found: C, 54.58; H, 8.37; N, 6.64.

Catalytic Reduction of Amino Acid Hydrochlorides (12) to Amino Acid Hydrochlorides (13).—The general procedure used was as follows. A mixture of 1.0 g of **12** in 75 ml of ethanol and 0.2 g of catalyst was hydrogenated in a Paar apparatus under 50 psi H_2 for 3 hr. The catalyst was filtered and the solvent was evaporated to dryness. The residue was washed with warm acetone to leave a quantitative yield of **13**. The catalyst for each hydrogenation is parenthetically noted.

Hydrogenation (PtO_2) of **12a** gave **3-amino-3-methyl-2-isopropylbutanoic acid hydrochloride (13a)**: mp 209° dec; ir (KBr), 5.73 μ (C=O).

Anal. Calcd for $C_8H_{18}NO_2Cl$: C, 49.10; H, 9.28; N, 7.16. Found: C, 49.39; H, 9.15; N, 7.21.

Hydrogenation (PtO_2) of **12b** gave **3-amino-2-ethyl-3-methylbutanoic acid hydrochloride (13b)**: mp 111–115° dec; ir (KBr) 5.85 μ (C=O).

Anal. Calcd for $C_7H_{16}NO_2Cl$: C, 46.28; H, 8.88; N, 7.71. Found: C, 45.96; H, 9.24; N, 7.80.

Hydrogenation (5% Pd–C) of **12d** gave **3-amino-2,3-dimethylbutanoic acid hydrochloride (13d)**: mp 125–130° dec; ir (KBr), 5.88 μ (C=O).

Anal. Calcd for $C_6H_{14}NO_2Cl$: C, 42.99; H, 8.42; N, 8.36. Found: C, 42.52; H, 8.59; N, 8.31.

Hydrogenation (5% Pd–C) of **12e** gave **2-(1-aminocyclohexyl)-propanoic acid hydrochloride (13e)**: mp 209° dec; ir (KBr), 5.88 μ (C=O).

Anal. Calcd for $C_9H_{18}NO_2Cl$: C, 52.04; H, 8.74; N, 6.74. Found: C, 51.98; H, 8.88; N, 6.68.

Hydrogenation (10% Pd–C) of **12f** gave *erythro*-**3-amino-2-benzyl-3-phenylpropanoic acid hydrochloride** (*erythro* **13f**): mp 236–237° dec; ir (KBr), 5.80 and 5.88 μ (C=O). This compound could not be obtained sufficiently pure for analysis.

Compound **13f** was also obtained by hydrogenation (10% Pd–C) of **9f** to *cis*-**3-benzyl-4-phenyl-2-azetidinone** (*cis* **18f**) (95%) which was quantitatively converted into **13f** by treatment with concentrated HCl. Compound *cis* **18f** had the following properties: mp 121–122° (from hexane); ir (KBr), 5.70 μ

(C=O); nmr ($CDCl_3$), δ 8.40 (broad singlet, 1, NH) 7.50–6.70 (multiplet with main peak at 7.29, 10, C_6H_5), 4.82 (d, 1, J = 5.5 Hz, CH) 4.05–3.55 (m, 1, $CHCH_2$), 2.58 (eight lines, the AB portion of an ABX pattern, 2, J_{AB} = 15 Hz, J_{BX} = 7 Hz, J_{AX} = 9 Hz, $\Delta\nu_{AB}$ = 22 Hz, CH_2).

Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.05; H, 6.62; N, 5.90.

Hydrogenation (PtO_2) of **12g** gave a 63:37 mixture of *erythro*- and *threo*-**3-amino-2-methyl-3-phenylpropanoic acid hydrochloride** (**13g**) as shown by nmr comparison with authentic samples: mp 200–201° dec; ir (KBr) 5.80 μ (C=O).

Anal. Calcd for: $C_{10}H_{14}NO_2Cl$: C, 55.69; H, 6.54; N, 6.49. Found: C, 55.60; H, 6.40; N, 6.40.

Hydrogenation (PtO_2) of **12h** gave **2-aminocyclonanecarboxylic acid hydrochloride** (**13h**): mp 214–215°; ir (KBr), 5.88 μ (C=O).

Anal. Calcd for $C_{10}H_{20}NO_2Cl$: C, 9.09; H, 54.17; N, 6.32. Found: C, 9.10; H, 53.80; N, 6.36.

Catalytic Reduction of Carboxamido-1,3-butadienes (10) to Saturated Amides (15).—Quantities of reactants and reductive and work-up procedures were the same as those in the quantitative conversion of **12** into **13**.

Hydrogenation (PtO_2) of **10a** gave **diisopropylacetamide** (**15a**): mp 147–148° (from ether–hexane) (lit.[8] mp 148–148.5°); ir (KBr), 6.06 μ (C=O).

Hydrogenation (PtO) of **10b** gave **2-isopropylbutanamide** (**15b**): mp 130–131° (from ether–hexane) (lit.[9] mp 133–134°); ir (KBr), 6.08 μ (C=O).

Hydrogenation (PtO_2) of **10c** gave **2-ethylbutanamide** (**15c**): mp 107–108° (from ether–hexane) (lit.[10] mp 107°); ir (KBr) 6.06 μ (C=O).

Hydrogenation (5% Pd–C) of **10d** gave 2,3-dimethyl-2-butenamide (**14d**) (85%) and **2,3-dimethylbutanamide** (**15d**) (15%). Both **10d** and **14d** were quantitatively reduced to **15d** using PtO_2 catalyst. Compound **14d** had the following properties: mp 128–129° (from ether–hexane) (lit.[23] mp 130.5°); uv max (CH_3OH), 218 mμ (ϵ 3700); ir (KBr), 6.02 μ (C=O). Evaporation to dryness of the mother liquors from the ether–hexane recrystallization gave **15d**: mp 129° (from ether–hexane) (lit.[11] mp 129°); ir (KBr), 6.03 μ (C=O).

Hydrogenation (5% Pd–C) of **10e** gave **2-cyclohexylpropanamide** (**15e**): mp 156–157° (from ether–hexane) (lit.[12] mp 156–157°); ir (KBr), 6.06 μ (C=O).

Reactions of CSI with Olefins (16).—The general procedure used was the same as for the reaction of CSI with allenes. Solid residues were recrystallized while the purity of liquids was checked by gas chromatography.

The combined aqueous extracts were extracted for 4–5 days (Raab extractor) with CH_2Cl_2. The CH_2Cl_2 extract was evaporated to dryness, and the residue was recrystallized to give **19**.

Variations in solvents and work-up procedure are noted under each olefin.

2,4-Dimethyl-2-pentene (**16a**) (10 g, 0.10 mol) gave 20.6 g (87%) of **1-chlorosulfonyl-4,4-dimethyl-3-isopropyl-2-azetidinone** (**17a**): mp 55–56° (from hexane); ir (KBr), 5.57 μ (C=O).

Anal. Calcd for $C_8H_{14}NO_3Cl$: C, 40.08; H, 5.89; N, 5.84. Found: C, 40.50; H, 5.83; N, 6.36.

3-Methyl-2-iospropyl-3-butenamide (**19a**) (0.5 g, 4%) had mp 123–124° (from ether–hexane); ir (KBr), 6.04 μ (C=O).

Anal. Calcd for $C_8H_{15}NO$: C, 67.98; H, 10.71; N, 9.92. Found: C, 68.04; H, 10.97; N, 10.06.

2-Methyl-2-pentene (**16b**) (20 g, 0.24 mol) gave 46 g (87%) of **1-chlorosulfonyl 3-ethyl-4,4-dimethyl-2-azetidinone** (**17b**), a liquid which showed a single peak on vpc but decomposed before elemental analyses could be obtained: ir (neat), 5.50 μ (C=O).

2-Ethyl-3-methyl-3-butenamide (**19b**) (3.0 g, 6%) had mp 58–60° (from ether–hexane); ir (KBr), 6.05 μ (C=O).

Anal. Calcd for $C_7H_{13}NO$: C, 66.10; H, 10.30; N, 11.01. Found: C, 65.91; H, 10.52; N, 11.29.

2-Methyl-2-butene (**16d**) (10 g, 0.14 mol) gave 21.1 g (70%) of **1-chlorosulfonyl-3,4,4-trimethyl-2-azetidinone** (**17d**): mp 44–45° (from 30–60° petroleum ether) (lit.[24] mp 44–45°); ir (KBr), 5.52 μ (C=O).

2-Methyl-3-methylenebutanamide (**19d**) (1.3 g, 8%) had mp 100–101° (from ether–hexane) (lit.[23] mp 104–105°); ir (KBr), 6.02 μ (C=O).

Ethylidenecyclohexane (**16e**) (11 g, 0.10 mol) gave 23.5 g (94%) of **1-chlorosulfonyl-3-methyl-1-azaspiro[3.5]nonan-2-one** (**17e**). After the addition of **16e** to CSI, both in ether solvent, **17e** precipitated and was filtered. Evaporation of the filtrate gave additional amounts of **17e**: mp 89–90° (from hexane); ir (KBr), 5.51 μ (C=O).

Anal. Calcd for $C_9H_{14}NO_3SCl$: C, 42.94; H, 5.61; N, 5.56. Found: C, 43.15; H, 5.62; N, 5.60.

trans-**1,3-Diphenylpropene** (**16f**) (4.0 g, 0.028 mol) gave 6.2 g (68%) of **1-chlorosulfonyl-*trans*-3-benzyl-4-phenyl-2-azetidinone** (**17f**). The solvent used was methylene chloride. After the usual work-up, the residue was extracted with seven 20-ml portions of boiling pentane and cooled: mp 65–66° (from pentane); ir (KBr), 5.50 μ (C=O).

Anal. Calcd for $C_{16}H_{14}NO_3SCl$: C, 57.23; H, 4.20; N, 4.17. Found: C, 57.04; H, 4.54; N, 4.33.

1-Chlorosulfonyl-*cis*-3-methyl-4-phenyl-2-azetidinone (*cis* **17g**).—A solution of 6.0 g (0.05 mol) of *cis*-β-methylstyrene (*cis* **16g**) in 10 ml of CH_2Cl_2 was added to a stirred solution of 7.1 g (0.05 mol) of CSI in 20 ml of CH_2Cl_2 at room temperature. The solution was stirred for an additional 5 hr and then poured onto 20 g of ice. The CH_2Cl_2 layer was separated and evaporated under a N_2 stream. The residue was dissolved in 50 ml of ether, decolorized twice with charcoal and filtered. Hexane (50 ml) was added to the filtrate and the solution was boiled until the temperature rose to 45°. Cooling led to the precipitation of the major portion of *cis* **17g** while further concentration of the mother liquor and cooling, yielded an additional amount: total yield 10.6 g (82%): mp 54–55°; ir (KBr), 5.51 μ (C=O).[25]

Anal. Calcd for $C_{10}H_{10}NO_3Cl$: C, 46.25; H, 3.88; N, 5.39. Found: C, 46.48; H, 4.09; N, 5.26.

1-Chlorosulfonyl-*trans*-3-methyl-4-phenyl-2-azetidinone (*trans* **17g**).—Similar treatment of *trans*-β-methylstyrene (*trans* **16g**) (6.0 g, 0.05 mol) gave 11.1 g (85%) of *trans* **17g**: mp 45–46°; ir (neat), 5.50 μ (C=O).[25]

Anal. Calcd for $C_{10}H_{10}NO_3SCl$: C, 46.25; H, 3.88; N, 5.39. Found: C, 46.49; H, 3.90; N, 5.71.

1-Chlorosulfonyl-*cis*-3,4-diethyl-2-azetidinone (*cis* **17i**).—The procedure used for the preparation of *cis* **17i** from ***cis*-3-hexane** (*cis* **16i**) was similar to that for *cis* **17g**, except for the reaction time (2 days) and solvent (50 ml of ether). The ether solution was extracted with seven 15-ml portions of water. The ether solution was dried (Na_2SO_4) and evaporated to dryness. The residue was extracted with four 30-ml portions of boiling petroleum ether (30–60°), and the resulting solution, cooling to −20°, deposited a major portion of *cis* **17i**. Concentration of the filtrate and again cooling to −20° led to additional amounts of *cis* **17i**. Thus 5.0 g (0.06 mol) of *cis* **16i** gave 6.3 g (47%) of *cis* **17i**. **N-chlorosulfonyl-β-lactam** *cis* **17i** is a liquid at room temperature; although vpc and nmr spectra of freshly prepared samples indicated a single product,[25] all attempts to obtain a sample of elemental analysis were frustrated by its ease of decomposition: ir (CCl_4), 5.49 μ (C=O).

1-Chlorosulfonyl-*trans*-3,4-diethyl-2-azetidinone (*trans* **17i**).—***trans*-3-Hexene** (*trans* **16i**) (10 g, 0.12 mol) gave, after a reaction time of 48 hr (24 hr at room temperature and 24 hr at a gentle reflux), 20.1 g (74%) of liquid *trans* **17i**: ir (CCl_4), 5.49 μ (C=O).[25]

The aqueous extracts from *cis* and *trans* **17i** gave, respectively, 0.3 g (4%) and 0.5 g (3%) of **2-ethyl-3-pentenamide** (**19i**): mp 76–77° (from hexane); ir (KBr), 6.01 μ (C=O).

Anal. Calcd for $C_7H_{13}NO$: C, 66.10; H, 10.30; N, 11.01. Found: C, 66.21; H, 10.45; N, 11.26.

Benzenethiol–Pyridine Reduction of N-Chlorosulfonyl-β-Lactams (17) to β-Lactams (18).—The procedure used was similar to that employed in the reduction of **8** to **9**.

Compound **17a** (19 g, 0.077 mol) gave 7.7 g (72%) of **4,4-dimethyl-3-isopropyl-2-azetidinone** (**18a**): mp 58–59° (from hexane); ir (KBr), 5.69 and 5.82 μ (C=O).

Anal. Calcd for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92. Found: C, 68.21; H, 10.87; N, 9.86.

Compound **17b** (22 g, 0.20 mol) gave 8.3 g (65%) of **3-ethyl-4,4-dimethyl-2-azetidinone** (**18b**): bp 64–66° (0.2 mm); ir (neat), 5.75 μ (C=O).

Anal. Calcd for $C_7H_{13}NO$: C, 66.10; H, 10.30; N, 11.01. Found: C, 65.91; H, 10.26; N, 11.12.

Compound **17d** (10.6 g, 0.05 mol) gave 3.1 g (50%) of **3,4,4-trimethyl-2-azetidinone** (**18d**): bp 62–63° (0.4 mm) (lit.[24] bp 74–75° (0.5 mm)); ir, 5.78 μ (C=O).

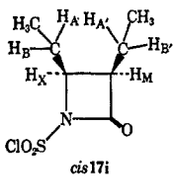
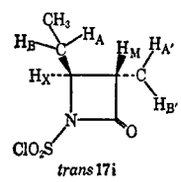
(23) E. J. Corey, *J. Amer. Chem. Soc.*, **75**, 1163 (1955).

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

(25) All nmr data are summarized in Table I.

TABLE I

NMR DATA OF *cis* AND *trans* **17g** AND *cis* AND *trans* **17i**[a]

Compd	Substituent	Chemical shift (δ)	Area	Multiplicity	Coupling constant, Hz
cis **17g**	R_1 (H_X)	5.52	1	Doublet	$J_{MX} = 7.25$
	R_2	7.42	5	Singlet	
	R_3	0.94	3	Doublet	$J_{AM} = 7.50$
	R_4 (H_M)	3.92	1	Pentet	
trans **17g**	R_1 (H_X)	4.89	1	Doublet	$J_{MX} = 4.00$
	R_2	7.49	5	Singlet	
	R_3 (H_M)	3.51	1	Quartet of doublets	
	R_4	1.50	3	Doublet	$J_{AM} = 7.60$
 *cis* **17i**	R_1 (H_X)	4.32	1	Six peaks[b]	$J_{AX} = J_{MX} = 7.50$, $J_{BX} = 5.75$
	CH_2's in R_2, R_3	2.20–1.50	4	Multiplet	
	CH_3's in R_2, R_3	1.30–0.80	6	Multiplet	
	R_4 (H_M)	3.52	1	Quartet[c]	$J_{A'M} = J_{B'M} = J_{MX} = 7.50$
 *trans* **17i**	R_1 (H_X)	4.00	1	Pentet[d]	$J_{AX} = 7.50$, $J_{BX} = J_{MX} = 3.75$
	CH_2's in R_2, R_4	2.30–1.60	4	Multiplet	
	CH_3's in R_2, R_4	1.40–0.80	6	Multiplet	
	R_3 (H_M)	3.16	1	Triplet of doublets	$J_{A'M} = J_{B'M} = 7.50$

[a] Spectra were determined in $CDCl_3$ (*cis* and *trans* **17g**) and CCl_4 (*cis* and *trans* **17i**); δ values are reported with an accuracy of ± 0.005 ppm while J values have an accuracy of ± 0.05 Hz. [b] Actually an ABMX pattern where two pairs of lines overlap giving the observed six lines. [c] Actually an A_2MX pattern where $J_{AM} = J_{MX}$; thus the eight expected lines overlap to give the observed quartet. [d] Actually an ABMX pattern where $J_{BX} = J_{MX} = J_{AX/2}$; thus the eight expected lines overlap to give the observed pentet.

Compound **17e** (20 g, 0.08 mol) gave 10.8 g (71%) of **3-methyl-1-azaspiro[3.5]nonan-2-one (18e)**: mp 62–63° (from hexane); ir (KBr), 5.68 and 5.75 μ (C=O).

Anal. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.85; H, 9.82; N, 8.96.

Compound *trans* **17f** (1.0 g, 0.003 mol) gave 0.65 g (93%) of ***trans*-3-benzyl-4-phenyl-2-azetidinone (*trans* 18f)**: mp 141–142° from ether–hexane); ir (KBr), 5.71 and 5.82 μ (C=O); nmr (DMSO-d_6), δ 7.75–6.90 (multiplet with main peak at 7.27, 11, C_6H_5 and NH), 4.42 (d, 1, J = 2 Hz, CHC_6H_5), 3.50–2.85 (m, 1, CH), and 3.18 (d, 2, J = 2 Hz, CH_2).

Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.27; H, 6.26; N, 5.70.

Compound *cis* **17g** (3.9 g, 0.015 mol) gave 2.3 g (96%) of ***cis*-3-methyl-4-phenyl-2-azetidinone (*cis* 18g)** after extraction of the residue with four 15-ml portions of boiling hexane followed by cooling of the extracts to −20°: mp 105–106°; ir (KBr), 5.68 and 5.88 μ (C=O).

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.37; H, 7.07; N, 8.68.

Compound *trans* **17g** (3.9 g, 0.015 mol) gave 2.1 g (87.5%) of ***trans*-3-methyl-4-phenyl-2-azetidinone (*trans* 18g)** using the same isolation procedure as for *cis* **18g**: mp 99–100°; ir (KBr), 5.68 and 5.82 μ (C=O).

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.63; H, 6.91; N, 8.47.

Compound *cis* **17i** (4.5 g, 0.02 mol) gave 1.7 g (68%) of ***cis*-3,4-diethyl-2-azetidinone (*cis* 18i)** after extraction of the residue with five 30-ml portions of boiling hexane followed by evaporation of the hexane extracts to a volume of 40 ml and cooling to −20°: mp 49–50°; ir (CCl_4), 5.67 and 5.70 μ (C=O).

Anal. Calcd for $C_7H_{13}NO$: C, 66.10; H, 10.30; N, 11.01. Found: C, 65.91; H, 10.28; N, 10.75.

Compound *trans* **17i** (4.5 g, 0.02 mol) gave 2.1 g (80%) of ***trans*-3,4-diethyl-2-azetidinone (*trans* 18i)** after evaporation of the hexane extracts followed by distillation *in vacuo*: bp 72–73° (0.3 mm); ir (CCl_4), 5.63 and 5.70 μ (C=O).

Anal. Calcd for $C_7H_{13}NO$: C, 66.10; H, 10.30; N, 11.01. Found: C, 65.88; H, 10.33; N, 11.34.

Concentrated Hydrochloric Acid Hydrolysis of β-Lactams 18 to Amino Acid Hydrochlorides (13).—The general procedure used was the same as that for the conversion of **9** into **12**. Thus **18a, 18b, 18d, 18e,** *trans* **18f,** *cis* **18g,** *trans* **18g,** *cis* **18i,** and *trans* **18i** were quantitatively and respectively converted into **13a, 13b, 13d, 13e,** *threo* **13f,** *erythro* **13g,** *threo* **13g,** *meso* **13i,** and *dl* **13i.**

***threo*-3-Amino-2-benzyl-3-phenylpropanoic acid hydrochloride (*threo* 13f)** had mp 227° dec (after boiling acetone wash); ir (KBr), 5.83 μ (C=O).

Anal. Calcd for $C_{16}H_{18}NO_2Cl$: C, 65.86; H, 6.22; N, 4.80. Found: C, 65.71; H, 6.44; N, 4.72.

***erythro*-3-Amino-2-methyl-3-phenylpropanoic acid hydrochloride (*erythro* 13g)** had the following properties: mp 221–223° dec; ir (KBr), 5.85 and 6.03 μ (C=O); nmr (D_2O), δ 7.41 (s, 5, C_6H_5), 4.50 (d, 1, J = 8 Hz, CHC_6H_5) 3.20 (rough pentet, 1 J = 7 Hz, $CHCH_3$), and 1.23 (d, 3, J = 7 Hz, CH_3).

Anal. Calcd for $C_{10}H_{14}NO_2Cl$: C, 55.69; H, 6.54; N, 6.49. Found: C, 55.44; H, 6.68; N, 6.50.

***threo*-3-Amino-2-methyl-3-phenylpropanoic acid hydrochloride (*threo* 13g)** had the following properties: mp 243–244° dec; ir (KBr), 5.80 μ (C=O); nmr (D_2O), δ 7.48 (s, 5, C_6H_5), 4.53 (d, 1, J = 10 Hz, CHC_6H_5), 3.40–2.80 (m, 1, $CHCH_3$), and 1.00 (d, 3, J = 7 Hz, CH_3).

Anal. Calcd for $C_{10}H_{14}NO_2Cl$: C, 55.69; H, 6.54; N, 6.49. Found: C, 55.71; H, 6.76; N, 6.26.

***meso*-3-Amino-2-ethylpentanoic acid hydrochloride (*meso* 13i)** had mp 175–176° dec; ir (KBr), 5.89 μ (C=O).

Anal. Calcd for $C_7H_{16}NO_2Cl$: C, 46.28; H, 8.88; N, 7.71. Found: C, 45.98; H, 8.87; N, 7.50.

***dl*-3-Amino-2-ethylpentanoic acid hydrochloride (*dl* 13i)** had mp 215–216° dec; ir (KBr), 5.86 μ (C=O).

Catalytic Reduction of β,γ-Unsaturated Amides (19) to Amides (15).—The general procedure used was the same as that for the conversion of **10** into **15**. Thus **9a, b, d,** and **i** were quantitatively and respectively converted into **15a, b, d,** and **i.**

Preparation of 3-Methyl-2-methylenebutanamide (20).—3-Methyl-2-methylenebutanoic acid (5.0 g) and thionyl chloride (7 g) were refluxed for 1 hr, followed by evaporation of the excess $SOCl_2$. The crude acid chloride was slowly added to 15 ml of 28% aqueous NH_3 maintaining the reaction temperature at 0°. The crude amide was filtered and dissolved in ether; the ethereal solution was dried ($MgSO_4$) and filtered, and 40 ml of hexane was added. The resulting solution was boiled until crystallization commenced, and then cooled to give 3.1 g (62%) of **20**: mp 103–104° (lit.[26] mp 104–105°); ir (KBr) 6.07 μ (C=O).

(26) V. P. Golmov and N. M. Afan'ev, *Zh. Obshch. Khim.*, **22**, 1953 (1952); *Chem. Abstr.*, **47**, 9269b (1953).

Treatment of either **19d** or **20** (1 g) in 10 ml of ethanol with 0.2 g of 5% Pd–C for 5 hr led only to recovery of starting material. Introduction of hydrogen into the system (50 psi) resulted in the quantitative conversion of both **19d** and **20** into **15d** in 15 min.

Ozonation of 1-Chlorosulfonyl-4,4-dimethyl-3-methylene-2-azetidinone (8d).—Excess ozone was bubbled through a cooled (−78°) solution of 0.523 g (2.50 mmol) of **8d** in 100 ml of CH_2Cl_2 with absorption of only 1.37 mmol of ozone. The solution was warmed to ambient temp, 25 ml of water was added and the two-phase system was refluxed overnight. The water layer was separated and added to 75 ml of a 10% alcoholic solution of 2,4-DNP·HCl. The precipitated product was filtered and recrystallized from methanol–water to give formaldehyde 2,4-dinitrophenylhydrazone, mp 166° (lit.[27a] mp 166°).

Diels–Alder Adduct of 3-Methyl-2-methylene-3-butenamide (10d).—An admixture of solutions of 1.1 g (0.01 mol) of **10d** in 20 ml of ether and 1.1 g (0.01 mol) of maleic anhydride in 30 ml of ether precipitated, after standing overnight, 1.9 g (90%) of **1-carboxamido-2-methyl-1-cyclohexene-4,5-dicarboxylic anhydride**: mp 160–161° (after cold acetone wash); ir (KBr), 5.41 and 5.73 (anhydride C=O) and 6.10 μ (amide C=O).

Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.70. Found: C, 57.50; H, 5.43; N, 6.44.

1-(2-Carboxy-3-methyl-2-butenyl)urea (22).—Pyridine (4.0 g, 0.05 mol) in 20 ml of acetone was added (30 min) to a cooled (−30°) and stirred solution of 10.4 g (0.04 mol) of **1-chlorosulfonyl-1-(2-carboxy-3-methyl-2-butenyl)urea (11)** and 8.8 g (0.08 mol) of benzenethiol in 100 ml of acetone. The solution was stirred for an additional 30 min at −30°. Addition of 150 ml of petroleum ether (30–60°) precipitated a semisolid product which was filtered and washed several times with petroleum ether and then dissolved in 40 ml of hot water. The hot solution was decolorized (charcoal) and cooled to crystallize 4.5 g (70%) of **22**. One recrystallization from acetone gave **22**: mp 177–178°; uv max (CH_3OH), 217 mμ (ε 8000); ir (KBr) 5.98 and 6.10 μ (C=O).

Anal. Calcd for $C_7H_{12}N_2O_3$: C, 48.83; H, 7.02; N, 16.27. Found: C, 49.00; H, 7.19; N, 15.98.

Ozonation of 11.—Excess ozone (6 mmol) was bubbled through a cooled solution (−78°) of 1.4 g (5.2 mmol) of **11** in 100 ml of ethyl acetate. The solution was then flushed with nitrogen and warmed to ambient temperature; 25 ml of water was added and the two phase system was refluxed overnight. After cooling, the water layer was separated and added to a 10% ethanolic solution of 2,4-DNP·HCl. After 1 hr, the crude hydrazone was filtered and recrystallized from methanol–water to give 0.25 g (20%) of acetone 2,4-dinitrophenylhydrazone, mp 128° (lit.[27b] mp 126°).

Oxidation of 22 with $KMnO_4$–$NaIO_4$.—To a potassium carbonate buffered (pH ~8) solution of 0.86 (0.005 mol) of **22** in 75 ml of water was added 80 ml of an oxidation mixture composed of 0.31 g of $KMnO_4$ and 21.0 g of $NaIO_4$ in 200 ml of water. The mixture was stirred for 90 min at room temperature after which 15 g of $NaHSO_3$ was added to destroy excess oxidant. The solution was warmed to 80° and a nitrogen stream was dispersed into the solution exiting into 25 ml of 10% ethanolic 2,4-DNP·HCl solution. The stream was continued until no more precipitate formed. The crude material was filtered and recrystallized from methanol–water to give 0.9 g (74%) of acetone 2,4-dinitrophenylhydrazone, mp 127–128°.

1-(2-Carboxy-3-methylbutyl)urea (23).—Hydrogenation (0.1 g PtO_2) of **22** (2 g) in 100 ml of ethanol in a Paar apparatus under 50 psi of hydrogen (4 hr) gave **23**: mp 131–132° (from acetone); ir (KBr), 5.83 and 6.09 μ (C=O).

Anal. Calcd for $C_7H_{14}N_2O_3$: C, 48.26; H, 8.10; N, 16.08. Found: C, 48.57; H, 8.08; N, 15.91.

2-Carboxy-3-methylbutylamine (24).—A solution of **23** in 30 ml of 25% aqueous KOH was refluxed 12 hr. After cooling and neutralization with concentrated HCl, the solution was evaporated to dryness *in vacuo*. The residue was extracted with two 25-ml portions of boiling absolute ethanol and the ethanol extracts also were evaporated to dryness. The residue was again extracted with boiling absolute ethanol. Evaporation of this ethanolic solution led to **24** (0.40 g, 15%): mp 215° dec; ir (KBr), 6.18, 6.40, and 6.68 μ (CO_2^- and $^+NH_3$).

(27) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, Inc., New York, N. Y., 1958: (a) p 283; (b) p 316.

1-Benzamido-2-carboxy-3-methylbutane (25).—A 25% aqueous KOH solution (30 ml) was added (15 min) to a stirred solution composed of 1.0 g of **24** and 1.5 g of benzoyl chloride. Stirring was continued for an additional 15 min, after which the solution was acidified to pH 4 (congo red) and cooled. The solution was extracted with three 20-ml portions of ether; the combined ether extracts were dried ($MgSO_4$) and 40 ml of hexane was added. The solution was evaporated slowly (steam bath) until the cloud point. On cooling 0.9 g (51%) of **25** crystallized: mp 174–175°; ir (KBr), 5.91 (acid C=O) and 6.12 μ (amide C=O).

Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.33; H, 7.47; N, 6.11.

1-Benzamido-2-carboxy-3-methyl-2-butene (27).—Urea **22** (2.4 g) was refluxed (12 hr) in 25 ml of 30% aqueous KOH to give an aqueous solution of the salt of **1-amino-2-carboxy-3-methyl-2-butene (26)**.[28] Benzoylation of **26** was accomplished in the same manner as the preparation of **25** to give 2.4 g of **27**. Benzoylation of the water layer (after the ether extraction) ultimately led to an additional 0.2 g of **27**: total yield 77%; mp 149–150°; uv max (CH_3OH), 225 mμ (ε 18,000); ir (KBr), 5.98 and 6.20 μ (C=O).

Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.93; H, 6.72; N, 5.98.

Hydrogenation (PtO_2) of **27** quantitatively converted it into **25**. Further, hydrogenation (PtO_2) of **22**, followed successively by saponification with aqueous KOH and treatment with benzoyl chloride, also led to **25** in 47% over-all yield.

Preparation of 25 from Diethyl Isopropylmalonate (28).—Saponification of 200 g (0.99 mol) of **28** in 650 ml of absolute ethanol with 60 g (1.07 mol) of KOH in an equal volume of the same solvent led ultimately to 151 g (88%) of ethyl isopropylmalonic acid ester (**29**) as an oil[29] which was used without further purification.

Diethylamine (62 g, 0.85 mol) was added slowly with stirring to 146 g (0.85 mol) of **29** at 0° followed by more rapid addition of 85 ml of 40% aqueous CH_2O solution (1.0 mol). After several hours, the solution clouded and CO_2 began to evolve slowly. After 24 hr, the two-phase system was separated, and the lighter moiety was dissolved in 50 ml of ether and dried ($MgSO_4$). Evaporation of the ether followed by distillation *in vacuo* gave 73 g (60%) of **ethyl 3-methyl-2-methylenebutanoate (30)**, bp 57–58° (932 mm) (lit.[30] bp 150°). Saponification of 20 g (0.16 mol) of **30** with 20 g of KOH in 125 ml of water led, after acidification, to 15.5 g (97%) of **3-methyl-2-methylenebutanoic acid (31)**, bp 71–72° (4 mm) (lit.[30] bp 100° (19 mm)).

Anhydrous hydrogen bromide was bubbled slowly into a solution of 5.0 g of **31** in 30 ml of $CHCl_3$ until an ir spectrum of the solution showed the absence of the C=C absorption at 6.15 μ (*ca.* 6 hr). The chloroform solution was evaporated *in vacuo* leaving the crude **2-bromomethyl-3-methylbutanoic acid (32)** as an oil which was used without further purification. This crude material was dissolved in 50 ml of aqueous NH_3 (28%) and the tightly capped flask was stirred for 24 hr at 45–50°. The mixture was then evaporated to dryness *in vacuo;* the residue was extracted with two 30-ml portions of boiling absolute ethanol. This too was evaporated to dryness, and the resulting residue was dissolved in a minimum volume of hot absolute ethanol. Addition of ether to the cloud point of the ethanolic solution, followed by cooling, gave 3.7 g (65%) of **24**, mp 215°. Benzoylation of **24** gave **25**, identical in all respects with that obtained *via* the degradation of **11**.

Leuckart Reduction of Ethyl 2-Benzoylpropanoate (33).—A mixture of 20 g (0.097 mol) of **33**[31] and 25 g (0.40 mol) of ammonium formate was slowly heated in an oil bath to 185–190°, at which temperature it was maintained for 4 hr. The water formed was removed with a Dean–Stark apparatus. After cooling, the mixture was dissolved in 40 ml of ether and washed with four 50-ml portions of H_2O. The ether layer was then evaporated to dryness and 50 ml of concentrated HCl added to the residue. This mixture was refluxed 4 hr and evaporated *in vacuo*, and the residue was recrystallized from methanol–ether to give 4.1 g (18%) of *threo* **13g**, identical in all respects with that obtained from the hydrolysis of *trans* **18g**.

(28) This could be isolated in conventional fashion as the zwitterion of **26**, mp 238° dec.

(29) E. J. Corey, *J. Amer. Chem. Soc.*, **74**, 5897 (1952).

(30) G. Darzens, *Compt. Rend.*, **152**, 445 (1911).

(31) R. H. Kimball, G. D. Jefferson, and A. B. Pike, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York. N. Y., 1943, p 284.

Mannich Reaction on Benzylmalonic Acid (34).—A mixture of 30 g (0.16 mol) of **34** (K & K Laboratories), 16.6 g (0.20 mol) of benzaldehyde, and 20 ml of 10% alcoholic NH_3 was heated for 1 hr on a steam bath and then 3 hr at 130° in an autoclave. The mixture was then added to 100 ml of 30% aqueous K_2CO_3 solution and the whole was extracted with three 70-ml portions of ether. The aqueous residue was slowly acidified with concentrated HCl and, on cooling, precipitated 7 g (19%) of **2-benzylcinnamic acid** (**35**), mp 159–160° (from ethanol–water) (lit.[32] mp 160°). The aqueous filtrate was extracted with three 50-ml portions of ether. The ether extracts were dried ($MgSO_4$) and evaporated to dryness and the residue was recrystallized from ethanol–ether to give 8 g (18%) of a 58:42 *erythro–threo* mixture of **13f** as determined by nmr spectroscopy: mp 226–227° dec; ir (KBr), 5.87 and 5.90 μ (C=O).

Registry No.—**8a**, 13086-19-6; **8b**, 16934-01-3; **8d**, 13088-65-8; **8e**, 13085-96-6; **8f**, 16934-04-6; **8h**, 13085-97-7; **9a**, 13085-98-8; **9b** (*cis*), 16933-57-6; **9b** (*trans*), 16933-58-7; **9d**, 13085-95-5; **9e**, 13085-99-9; **9f**, 16933-61-2; **9g**, 16933-62-3; **9h**, 13086-00-5; **10a**, 16933-64-5; **10b** (*cis*), 16933-65-6; **10b** (*trans*), 16933-66-7; **10c**, 16933-67-8; **10d**, 13088-60-3; **10e**, 16933-69-0; **11**, 16933-70-3; **12a**, 16933-71-4; **12b**, 16933-72-5; **12d**, 16933-73-6; **12e**, 16933-74-7; **12f**, 16933-75-8; **12g**, 16933-76-9; **12h**, 16933-77-0; **13a**, 16933-78-1; **13b**, 16933-79-2; **13d**, 16933-80-5; **13e**, 16933-81-6; **13f** (*threo*), 16933-82-7; **13f** (*erythro*), 16933-83-8; **13g** (*threo*), 16933-84-9; **13g** (*erythro*), 16933-85-0; **13i** (*meso*), 16933-86-1; **13i** (*dl*), 16933-87-2; **17a**, 16933-88-3; **17e**, 16933-89-4; **17f**, 16933-90-7; **17g** (*cis*), 16933-91-8; **17g** (*trans*), 16933-92-9; **17i** (*cis*), 16933-93-0; **17i** (*trans*), 16933-94-1; **18a**, 16933-95-2; **18b**, 16933-96-3; **18e**, 16933-97-4; **18f** (*cis*), 16933-98-5; **18f** (*trans*), 16933-99-6; **18g** (*cis*), 16934-12-6; **18g** (*trans*), 16934-13-7; **18i** (*cis*), 16934-14-8; **18i** (*trans*), 16934-15-9; **19a**, 16934-16-0; **19b**, 16934-17-1; **19i**, 16934-18-2; **22**, 16934-19-3; **23**, 16934-20-6; **24**, 16934-21-7; **25**, 16934-22-8; **27**, 16934-23-9; 1-carboxamido-2-methyl-1-cyclohexene-4,5-dicarboxylic anhydride, 16934-24-0; chlorosulfonyl isocyanate, 1189-71-5.

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Azetidines. IV. The Reaction of 1,1-Dimethyl-, 1-Benzyl-1-methyl-, and 1,1-Dibenzyl-3,3-dimethylazetidinium Salts with Alkali Metal Amides in Liquid Ammonia[1-3]

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Of several possibilities, only the Stevens rearrangement product arising from enlargement of the azetidine ring was obtained from the reaction of 1,1,3,3-tetramethylazetidinium iodide (**1**) with potassium amide in liquid ammonia. Similarly, 1-benzyl-1,3,3-trimethylazetidinium iodide (**8**) gave only the ring-enlarged Stevens product even though, in this case, a Sommelet product was also possible. In contrast, 1,1-dibenzyl-3,3-dimethylazetidinium bromide (**13**) gave a 98% yield of the Sommelet product plus a small amount of the Stevens product with the azetidine ring retained. Ion-pair mechanisms best account for these results.

The reaction with sodium amide in liquid ammonia of tetraalkylammonium halides possessing a benzylic hydrogen was found by Kantor and Hauser[4] to be an excellent method for effecting the Sommelet rearrangement.[5] Subsequently Hauser and coworkers established, by two independent proofs,[6] that the mechanism for this reaction involved nucleophilic attack by an ylide carbon at the *ortho* position of the aromatic ring followed by tautomeric rearomatization.

The investigation of a number of quaternary salts of this type led to the implication that sodium amide in liquid ammonia was quite selective and gave exclusively either the Sommelet or the Stevens[7] (*e.g.*, with benzhydrylbenzyldimethylammonium ion[8]) rearrangement. More recent studies have shown that these early results were, at least in part, caused by a fortuitous choice of quaternary salts. Thus Jones, *et al.*,[9] Fery and Wilputte-Steinert,[10] Bumgardner,[11] and Jenny and Druey[12] have found examples in which the Stevens rearrangement accompanies the Sommelet rearrangement, and Klein and Hauser[13] have discovered that benzhydryltrimethylammonium ion, which had previously been reported to give only the Sommelet product, actually forms *ca.* 15% Stevens product.

The behavior of quaternary ammonium salts which do not possess a benzylic or similarly activated methylene group with alkali metal amides in liquid ammonia

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