stirred at room temperature for 15 hr. Evaporation of the volatile solvent, under reduced pressure, afforded a white solid which was recrystallized from methanol to afford 150 mg (54.5%) of colorless crystals, mp 138–143°. The infrared spectrum of this material proved to be identical with that of authentic *cis,trans,-cis*-tetracarbomethoxycyclobutane (**27**).[47]

Registry No.—**6**, 17072-56-9; **7**, 17062-18-9; **9**, 17278-20-5; **11**, 17062-19-0; **12**, 17072-57-0; **13**, 17062-20-3; **14**, 17062-21-4; **15**, 17062-22-5; **18**, 4430-15-3; **22**, 17088-18-5; **23**, 17062-24-7; **24**, 17062-25-8; **26**, 17062-26-9; **27**, 1032-95-7; **28**, 17062-28-1; **29**, 17062-29-2; **30**, 17062-30-5.

Acknowledgment.—We are indebted to the National Science Foundation (Grants G-13759, G.P. 3764, and G.P. 2543) for financial support of this work.

Olefinic Intermediates in the Reaction of 1,1-Dimethyl-, 1,1,2-Trimethyl-, and 1,1,2,2-Tetramethylcyclopropanes with Chlorosulfonyl Isocyanate[1,2]

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1,1-Dimethylcyclopropane (**1**) on treatment with chlorosulfonyl isocyanate (CSI) led to 1-chlorosulfonyl-3,4,4-trimethyl-2-azetidinone (**2**, 73%), and, from the aqueous extract, a mixture (5%) of equal amounts of 2,3-dimethyl-3-butenamide (**3**) and 2,3-dimethyl-2-butenamide (**4**). Treatment of 2-methyl-2-butene (**5**) gave **2** (70%) and **3** (8%). Similarly, 1,1,2-trimethylcyclopropane (**6**) and CSI led to 1-chlorosulfonyl-3,3,4,4-tetramethyl-2-azetidinone (**7**, 74%) as did 2,3-dimethyl-2-butene (**8**) and CSI in 86% yield. Finally, both 1,1,2,2-tetramethylcyclopropane (**9**) and 2,3,3-trimethyl-1-butene (**12**) with CSI produced 1-chlorosulfonyl-4-*t*-butyl-4-methyl-2-azetidinone (**10**) (65 and 67%, respectively) and 3,3-dimethyl-2-methylenepentanamide (**11**) (22 and 24%, respectively). The remarkable identity of both products and yields from **1** and **5**, **6** and **8**, and **9** and **12** suggests a slow rearrangement of cyclopropanes **1**, **6**, and **9** to their respective olefins, **5**, **8**, and **12**, catalyzed by the electrophile CSI. Subsequent CSI addition to rearranged olefin leading to β-lactam and unsaturated amide products can be regarded as fast. The cyclopropane → olefin rearrangement pathway was confirmed by CSI addition to 1,1,2,2-tetramethylcyclopropane-3,3-d_2 (**9**-d_2) which led ultimately to **17**-d_2 and **11**-d_2 in which the deuterium present is almost exclusively in one of the methyls of the *t*-butyl group.

In preceding studies, the propensity of chlorosulfonyl isocyanate[4] (CSI) to undergo predominantly cycloaddition reactions with olefins[5,6a–c] and allenes[6d,e] has been documented. In this paper, we wish to report the reaction of CSI with the title compounds leading to the same β-lactam and unsaturated amide products obtained from treatment of the appropriate olefin with CSI.

Results

1,1-Dimethylcyclopropane (**1**) reacted with CSI to give 1-chlorosulfonyl-3,4,4-trimethyl-2-azetidinone (**2**, 73%), and from the aqueous extract a mixture (5%) of equal amounts[7] of 2,3-dimethyl-3-butenamide (**3**)[6d,e] and 2,3-dimethyl-2-butenamide (**4**).[6d,e,8] 2-Methyl-2-butene (**5**) and CSI gave **2** (70%) and **3** (8%). Similarly, 1,1,2-trimethylcyclopropane (**6**) and 2,3-dimethyl-2-butene (**8**) reacted with CSI to give 1-chlorosulfonyl-3,3,4,4-tetramethyl-2-azetidinone (**7**) in 74 and 86% yield, respectively. Finally, the reaction of both 1,1,2,2-tetramethylcyclopropane (**9**) and 2,3,3-trimethyl-1-butene (**12**) with CSI produced 1-chlorosulfonyl-4-*t*-butyl-4-methyl-2-azetidinone (**10**) (65 and 67%, respectively) and 4,4-dimethyl-3-methylenepentamide (**11**) (22 and 24%, respectively) (Chart I). In general, the reactions between CSI and **1**, **6**, and **9** were run at room temperature in methylene chloride solvent and required 3–48 hr for completion; olefins **5**, **8**, and **12**, however, led to products at 0° in the same solvent within 30 min.

Benzenethiol–pyridine reduction of N-chlorosulfonyl-β-lactams **2**, **7**, and **10** in acetone led to the appropriate unsubstituted β-lactams **13**, **15**, and **17**, respectively; concentrated hydrochloric acid quantitatively converted these into amino acid hydrochlorides **14**, **16**, and **18**, respectively.

Mechanism.—Currently, three mechanisms seem operative in the electrophilic, ring opening of cyclopropanes. Using **9** as an exemplary substrate with the electrophile CSI (Chart II), these include the following: (a) initial electrophilic attack followed by cleavage "between those carbons which are united with the greatest and smallest number of alkyl residues," the nucleophile "attaching itself to that carbon atom (in **19**) which carries the most alkyl radicals;"[9] (b) acid-catalyzed rearrangement of cyclopropane **9** to **12**[8b,10,11] followed by the suggested[4,5] two-step addition[12] of CSI to **12** leading to products **10** and **11** *via* the

(1) This research was supported by Public Health Service Research Grant No. 1-R01-A1081063-01 from the National Institute of Allergy and Infectious Diseases.

(2) Presented before the Organic Division, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts, p P198.

(3) (a) Taken entirely from the Ph.D. Thesis of J. F. Kelly, 1968; (b) Department of Chemistry, Massachusetts Institute of Technology, National Institutes of Health Postdoctoral Trainee, 1967–1969 (GM 015230).

(4) R. Graf, *Ber.*, **89**, 1071 (1956); *Org. Syn.*, **46**, 23 (1966).

(5) R. Graf, *Ann.*, **661**, 111 (1963); *Org. Syn.*, **46**, 51 (1966).

(6) (a) E. J. Moriconi and P. H. Mazzocchi, *J. Org. Chem.*, **31**, 1372 (1966); (b) E. J. Moriconi and W. C. Crawford, *ibid.*, **33**, 370 (1968); (c) E. J. Moriconi and J. F. Kelly, *Tetrahedron Lett.*, 1435 (1968); (d) E. J. Moriconi and J. F. Kelly, *J. Amer. Chem. Soc.*, **88**, 3657 (1966); (e) E. J. Moriconi and J. F. Kelly, *J. Org. Chem.*, **33**, 3036 (1968).

(7) Determined by vpc.

(8) (a) Undoubtedly the product of partial isomerization of **3** on long standing under acidic conditions. (b) For a quite similar $\beta,\gamma \rightleftharpoons \alpha,\beta$ equilibration of unsaturated carbonyl compounds, see R. Ya. Levina, V. N. Kostin, P. A. Gembitski, and E. G. Treschova, *J. Gen. Chem. USSR*, **30**, 883 (1960).

(9) Comprehensively summarized by M. Yu. Lukina, *Russ. Chem. Rev.*, **31**, 419 (1962). See also R. J. Ouellette and D. L. Shaw, *J. Amer. Chem. Soc.*, **86**, 1651 (1964); R. J. Ouellette, R. O. Robins, and A. South, Jr., *ibid.*, **90**, 1619 (1968).

(10) R. Ya. Levina, V. N. Kostin, P. A. Gembitski, and E. G. Treschova, *J. Gen. Chem. USSR*, **30**, 868 (1960).

(11) H. Hart and G. Levitt, *J. Org. Chem.*, **24**, 1261 (1959).

(12) See ref 6b and c for possible exceptions.

CHART I

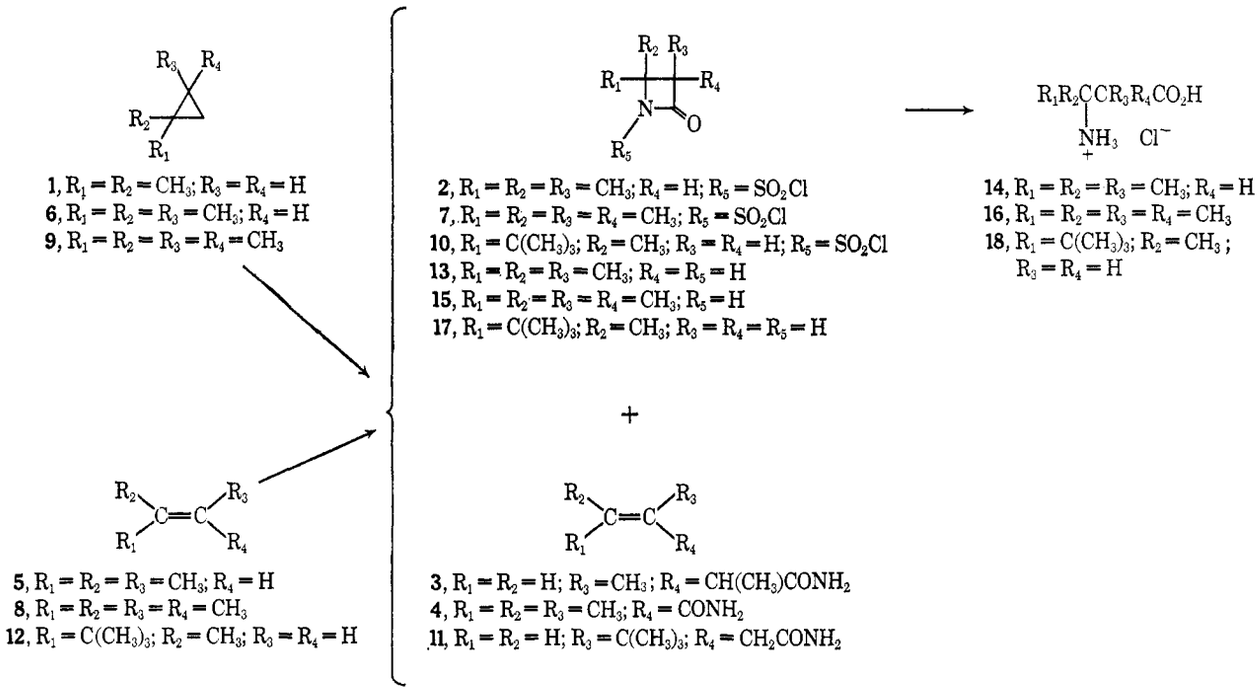
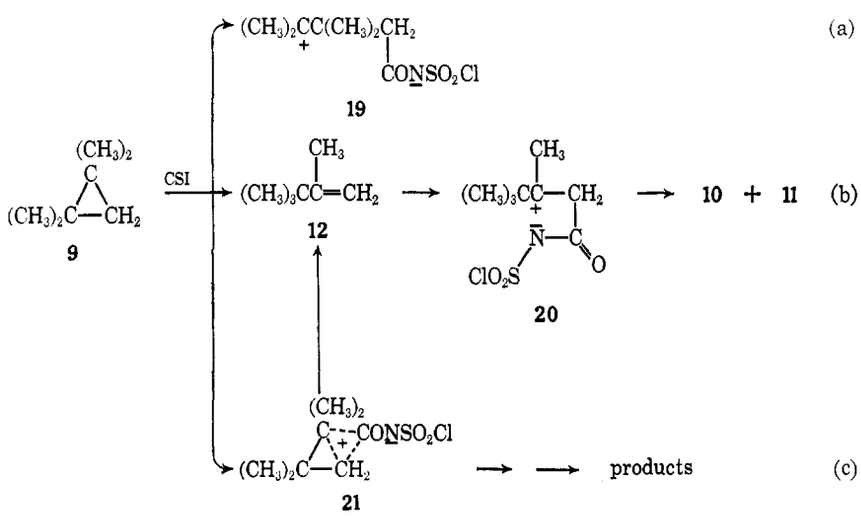
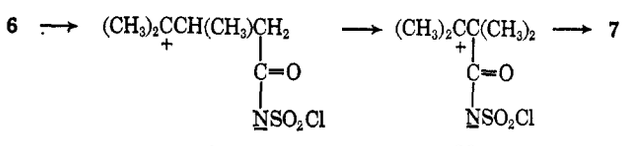


CHART II



"dipolar adduct" (**20**); and (c) formation of hydrogen or carbon bridged ions (*e.g.*, **21**) which could rearrange to **12** or lead to products in which the electrophilic and nucleophilic moieties are scrambled.[13]

The remarkable identity of β-lactam and unsaturated amide products and yields from both **1** and **5**, **6** and **8**, and **9** and **12** suggested, at the outset, a common intermediate between the appropriate cyclopropane and olefin enroute to products. The simplest of these that could be envisioned would be the 1,4 dipole arising directly from the reaction between CSI and olefin,[4,5,6d] *e.g.*, **20** from **12**, and **23** from **8**. The formation of these adducts, however, from cyclopropanes **9** and **6**, respectively, *via* path a, seemed doomed to a series of energetically unattractive (**19** → **20**) or irrational rearrangements (**22** → **23**) to account for β-lactam formation.



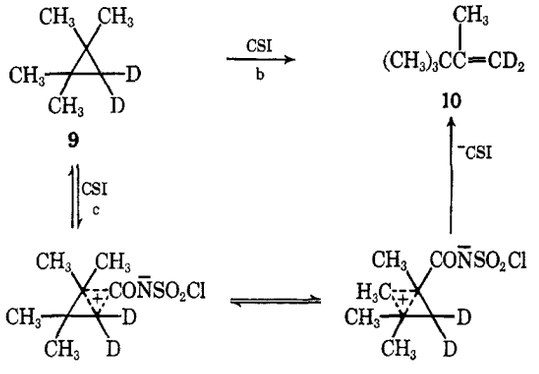
It seemed much more reasonable to postulate a precedented[8b,10] rearrangement (slow) of **1**, **6**, and **9** in the presence of CSI, to olefins **5**, **8**, and **12**, followed by cycloaddition (rapid) of CSI leading to the observed products. The literature records such a rearrangement of **9** to **12** on stirring with catalytic amounts of phosphoric acid or phosphoric acid–acetic anhydride. We were able to effect a similar rearrangement of **1** and **6** to **5** and **8**, respectively, under the same conditions. Further, we were encouraged in this direction by the discovery that **6** rearranged to **8** in the presence of **7**. Finally, although the cyclopropane → olefin rear-

(13) C. C. Lee and L. Gruber, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, p S81; H. Hart and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **88**, 5030 (1966); G. J. Karabatsos, N. Hsi, and S. Meyerson, *ibid.*, **88**, 5649, 5651 (1966); N. C. Deno and D. N. Lincoln, *ibid.*, **88**, 5357 (1966); R. L. Baird and A. A. Aboderin, *ibid.*, **86**, 252 (1964).

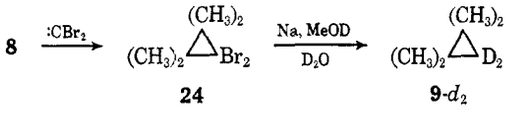
rangement seems to be catalyzed by pure CSI,[14] the presence of inorganic acids, even in freshly distilled CSI, accelerate the isomerization.

Unresolved then is the pathway by which the cyclopropane → olefin rearrangement might occur. Chart III delineates the route in pathways b and c by which this rearrangement could be achieved. Using **9** again as the substrate, it should be noted that, in path b, the ring methylene protons in **9** appear as part of a methyl in the *t*-butyl group of **10**; conversely, the vinyl protons in the latter originate from a methyl group in **9**. In path c, the ring methylene protons in **9** become the vinyl protons in **10**.[15]

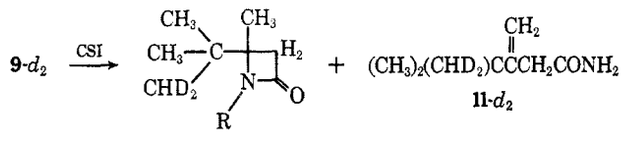
CHART III



A decisive resolution between these two specific pathways was obtained by the use of 1,1,2,2-tetramethylcyclopropane-3,3-d_2 (**9**-d_2) prepared *via* reduction



of its known dibromo precursor **24**.[16] Treatment of **9**-d_2 with CSI converted it into the expected products, **10**-d_2 and **11**-d_2. Benzenethiol–pyridine reduction of **10**-d_2 gave **17**-d_2. A mass spectral analysis of **17**, **17**-d_2, **11**, and **11**-d_2 indicated the deuterium to be present almost exclusively in one of the *t*-butyl methyls in both **17**-d_2 and **11**-d_2, lending full support to the olefinic intermediates and rearrangement suggested by path b. (See Table I.)



(14) In one experiment, anhydrous potassium carbonate was added to both the freshly distilled CSI (middle cut; under nitrogen) and **6** before admixture. The former was then added to the latter under nitrogen, and the reactants remained in contact with the solid potassium carbonate throughout the reaction period. Under these conditions, the reaction rate decreased eightfold, but products and yields remained the same.

(15) In both pathways, π complexes as precursors are not precluded.

(16) W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **76**, 6162 (1954).

Experimental Section[17]

Reaction of CSI with 1,1-Dimethylcyclopropane (**1**).—A solution of 23 g (0.33 mol) of **1** in 10 ml of CH_2Cl_2 was added to a solution of 42.3 g (0.30 mol) of CSI in 50 ml of CH_2Cl_2. The solution was stirred for 48 hr at room temperature and then slowly poured onto 50 g of ice. The CH_2Cl_2 layer was separated and the water was extracted with 20 ml of CH_2Cl_2. These extracts were combined and evaporated and the residue was dissolved in 100 ml of ether. This ether solution was extracted with seven 20-ml portions of water and then evaporated to dryness under a stream of nitrogen. The residue was extracted with five 50-ml portions of petroleum ether (30–60°). Cooling of this extract gave the crude **1-chlorosulfonyl-3,4,4-trimethyl-2-azetidinone** (**2**) which was purified *via* several recrystallizations from petroleum ether: mp 44–45° (lit.[5] mp 44–45°); yield 47.2 g (72.6%).

The combined aqueous extracts were in turn extracted for 4 days with methylene chloride in a Raab extractor. Evaporation of the methylene chloride and recrystallization of the residue from ether–hexane gave 1.8 g (5%) of an amide mixture shown by gas chromatography to be a mixture composed of approximately equal amounts of **3** and **4**.[6d,e]

Anal. Calcd for C_6H_9NO mixture: C, 63.73; H, 9.79; N, 12.38. Found: C, 63.51; H, 10.00; N, 12.08.

2-Methyl-2-butene (**5**) (10 g, 0.14 mol) gave 21.1 g (70%) of **2**, mp 44–45° (from 30–60° petroleum ether), and 1.3 g (8%) of **3**, mp 100–101° (from ether–hexane) (lit.[5] mp 104–105°).[6d,e]

Reaction of CSI with 1,1,2-Trimethylcyclopropane (**6**).—A solution of 19.5 g (0.23 mol) of **6** in 20 ml of CH_2Cl_2 was added slowly with stirring to an ice bath cooled solution of 28.2 g (0.20 mol) of CSI in 30 ml of CH_2Cl_2. The solution was then stirred for 3 hr after the addition and poured onto 30 g of ice. It was extracted once with water and then the CH_2Cl_2 solution was evaporated under a stream of N_2. The residue was recrystallized several times from 30–60° petroleum ether to give 33.5 g (74.4%) of **1-chlorosulfonyl-3,3,4,4-tetramethyl-2-azetidinone** (**7**): mp 62–64° (lit.[5] mp 66–67°); ir (KBr), 5.58 μ (C=O); nmr ($CDCl_3$), δ 1.67 [s, 6, $-N-C(CH_3)_2$] and 1.37 [s, 6, $-CO-C(CH_3)_2$].

Reaction of CSI with 2,3-Dimethyl-2-butene (**8**).—A solution of 33.6 g (0.4 mol) of **8** in 30 ml of CH_2Cl_2 was slowly added with stirring to an ice bath cooled solution of 56.4 g (0.40 mol) of CSI in 40 ml of CH_2Cl_2. The work-up was the same as for the reaction with **6** and CSI and led to 77.5 g (86.1%) of **8** with the same melting point and spectral characteristics as that obtained from **6**.

Reaction of CSI with 1,1,2,2-Tetramethylcyclopropane (**9**).—A solution of 2 g (0.020 mol) of **9** in 5 ml of dry CH_2Cl_2 was added slowly to a solution of 2.5 g (0.018 mol) of CSI in 10 ml of CH_2Cl_2. The solution was stirred overnight at room temperature and then the solvent was evaporated *in vacuo*. The residue was dissolved in 30 ml of ether and this solution was extracted with seven 15-ml portions of water. The ether was then evaporated under a stream of N_2 and the residue was extracted with boiling 30–60° petroleum ether. The petroleum ether was evaporated and the residue was again extracted with a minimum amount of petroleum ether. Cooling of this extract to −20° gave 3.1 g (65%) of **1-chlorosulfonyl-4-*t*-butyl-4-methyl-2-azetidinone** (**10**) as a liquid with a melting point of about −15°; ir (neat), 5.55 μ (C=O); nmr ($CDCl_3$), δ 3.17 (AB pattern, J_{AB} = 17 Hz, $\Delta\nu_{AB}$ = 16 Hz, CH_2), 1.87 (s, 3, CH_3), and 1.13 [s, 9, $C(CH_3)_3$].

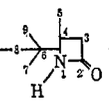
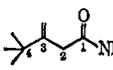
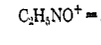
Anal. Calcd for $C_8H_{14}NO_3SCl$: C, 40.08; H, 5.88; N, 5.84. Found: C, 39.86; H, 5.91; N, 5.91.

The aqueous solution from the previous extraction with water was heated to 100° and 20 g of NaCl was added. After the NaCl dissolved, the solution was cooled to −10° to give 0.62 g (21.6%) of **4,4-dimethyl-3-methylenepentanamide** (**11**): mp 139–140°

(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. Mass spectra were determined on a CEC 21-104 spectrometer at 70 eV. Gas chromatograms were run on a Perkin Elmer 880 instrument with a flame ionization detector 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. Cyclopropanes **1**, **6**, and **9**, and olefins **5**, **8**, and **12** were obtained from Chemical Samples Co.

TABLE I

MASS SPECTRA OF 11, 17, 11-d_2 AND 17-d_2

	Ion fragments[a] (relative intensities)[b]							
								
m/e	**17**		**17-d_2**		**11**		**11-d_2**	
143			M^+	(3)			M^+	(25)
141	M^+	(22)		(0)	M^+	(18)		(0)
128		(0)	$[M - CH_3]^+$	(3.7)		(0)	$[M - CH_3]^+$	(42)
127		(0.3)		(0.4)		(5)		(9)
126	$[M - CH_3]^+$	(3)	$[M - CHD_2]^+$	(1.4)	$[M - CH_3]^+$	(50)	$[M - CHD_2]^+$ and $[M - NH_3]^+$	(20)
124		(0)		(0)	$[M - NH_3]^+$	(3)		
115			$[M - CO]^+$	(1.4)				
113	$[M - CO]^+$	(1.3)		(0)				
111						(0)	$[128 - NH_3]^+$	(6)
109					$[126 - NH_3]^+$	(8)		(3)
102			$[M - HC{\dot{=}}C{=}O]$	(2)				
100	$[M - HC{\dot{=}}C{=}O]$	(2.5)	$[M - NHCO]^+$	(6)		(1)		(7)
99					$[M - C_3H_6]^+$	(7)	$[M - C_3H_4D_2]^+$	(9)
98	$[M - NHCO]^+$	(6)						(4)
85		(9)		(41)		(4)		(100)[c]
84	$[M - C_4H_9]^+$	(100)[c]	$[M - C_4H_7D_2]^+$	(100)[c]		(26)		(28)
83		(44)		(16)	$C_6H_{11}^+$ = 	(100)[c]		(32)
71	$C_5H_{11}^+$ = 	(0.6)	$C_5H_7D_2^+$	(1.0)		(0)		(3)
69	$C_5H_9^+$ = 	(0.8)	$C_5H_5D_2^+$	(0.6)		(4)		(3.5)
68		(0.3)		(0.3)		(2)		(3)
67	$C_5H_7^+$ = 	(0.4)	$C_5H_3D_2^+$	(0.2)	$C_5H_7^+$ = 	(2.5)		(1)
60		(0)		(7)		(3)		(20)
59		(1)	$C_4H_7D_2^+$	(16)	$C_2H_5NO^+$ = 	(66)		(78)
58	$C_4H_{10}^+$	(7)	$C_4H_6D_2^+$ and $C_4H_8D^+$	(41)		(2)		(10)
57	$C_4H_9^+$ = 	(29)	$C_4H_5D_2^+$ and $C_4H_7D^+$	(18)	$C_4H_9^+$ =	(7.5)		(20)
56		(3)	$C_4H_6D^+$	(6)				(25)
55	$C_4H_7^+$ =	(11)		(4.5)	$C_4H_7^+$ =	(41)		(19)
44		(1)		(7)	$[H_2N^+{=}C{=}O]$	(12)		(16)
43	$[HN{=}C{=}O]^+$	(28)		(24)		(7)		(9)
42	$C_3H_6^+$ or $[NCO]^+$	(60)		(54)		(9)		(13)
41	$C_3H_5^+$ = 	(4)		(2.5)	$C_3H_5^+$ =	(10)		(7)

[a] Fragments retaining the amide functions were determined by doing a D_2O exchange and noting which peaks were shifted by 1 or 2 mass units. [b] Of the more important peaks. [c] Base peak.

(from ether) (lit.[5] mp 140–141°); ir (KBr), 2.98 and 3.14 (NH), 6.06 (C=O), and 6.18 μ (C=C and amide II); nmr (DMSO-d_6), δ 6.60 (broad singlet, 2, NH_2), 4.97 and 4.70 (two vinyl doublets, each allylically coupled to CH_2, J = 1 Hz, $=CH_2$), 2.87 (d, 2, J = 1 Hz, CH_2) and 1.03 [s, 9, $C(CH_3)_3$].

Reaction of CSI with 2,3,3-Trimethyl-1-butene (12).—A solution of 10 g of **12** (0.10 mol) in 15 ml of CH_2Cl was added slowly with stirring to an ice bath cooled solution of 14 g (0.099 mol) of CSI in 20 ml of CH_2Cl_2. The methylene chloride solution was stirred for an additional 15 min and evaporated *in vacuo*, and the residue was dissolved in 30 ml of ether. The solution was then extracted with seven 15-ml portions of water and the ether layer evaporated under a stream of N_2. The residue was worked up as in the reaction of CSI with **9** to give 16.0 g (67.5%) of **10**.

The water solution used to extract the ether layer above was worked up in the usual manner to give 3.2 g (24%) of **11**.

Benzenethiol–Pyridine Reduction of N-Chlorosulfonyl-β-lactams (2, 7, 10) to β-Lactams (13, 15, 17).—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 cyclopropane and benzenethiol (2 equiv) in acetone (40 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. Variations on final isolation procedures are noted under each β-lactam.

Compound **2** (10.6 g, 0.05 mol) gave 3.1 g (50%) of **3,4,4-trimethyl-2-azetidinone (13)** after distillation of the residual oil, bp 62–63° (0.4 mm)[6e] [lit.[5] bp 74–75° (0.5 mm)].

Compound **7** (11.3 g, 0.05 mol) gave 3.2 g (51%) of **3,3,4,4-tetramethyl-2-azetidinone (15)** after final extraction of the residue with three 25-ml portions of boiling hexane. Upon cooling the combined extracts to −20°, **15** crystallized: mp 100–101° (lit.[5] mp 104°); ir (KBr), 3.14 (NH), 5.74 and 5.85 μ (C=O); nmr ($CDCl_3$), δ 6.82 (broad singlet, 1, **NH**), 1.32 [s, 6, $-N-C(CH_3)_2$], and 1.20 [s, 6, $-CO-C(CH_3)_2$].

Compound **10** (12.5 g, 0.05 mol) gave 4.1 g (57%) of **4-*t*-butyl-4-methyl-2-azetidinone (17)** after final extraction of the residue with four 40-ml portions of boiling 30–60° petroleum ether. The volume of the combined extracts was reduced to 60 ml, after which cooling to −20° gave **17**: mp 139–146° [from petroleum ether and sublimation 50° (0.1 mm)]; vpc showed a single peak; ir (KBr), 3.10 (NH), 5.70 μ (C=O); nmr ($CDCl_3$), δ 7.45 (broad singlet, 1, **NH**), 2.69 (AB pattern, 2, J_{AB} = 14.5 Hz, $\Delta\nu_{AB}$ = 27 Hz, CH_2), 1.42 (s, 3, CH_3), and 0.98 [s, 9, $C(CH_3)_3$].

Anal. Calcd for $C_5H_{15}NO$: C, 68.04; H, 10.71; N, 9.92. Found: C, 68.25; H, 10.67; N, 10.00.

Concentrated Hydrochloric Acid Hydrolysis of β-Lactams (13, 15, 17) to Amino Acid Hydrochlorides (14, 16, 18).—The general procedure used was as follows. Concentrated HCl (2 ml/g) was added to analytically pure β-lactam and stirred for 30 min. The excess water and HCl were removed *in vacuo* and the residue was washed with cold acetone to give a quantitative yield of amino acid hydrochloride.

Compound **13** gave **3-amino-2,3-dimethylbutanoic acid hydrochloride (14)**, mp 125–130° dec (lit. mp 125–130° dec).[6e]

Compound **15** gave **3-amino-2,2,3-trimethylbutanoic acid hydrochloride (16)**: mp 234° dec; ir (KBr), 4.91 ($^+NH_3$), 5.90 (C=O) and 6.20 μ (NH); nmr (D_2O), δ 1.35 [s, 6, $\geqslant N^+-C(CH_3)_2$] and 1.24 [s, 6, $-CO-C(CH_3)_2$].

Anal. Calcd for $C_7H_{16}NO_2Cl$: C, 46.28; H, 8.88; N, 7.47. Found: C, 46.34; H, 8.98; N, 7.71.

Compound **17** gave **3-amino-3,4,4-trimethylpentanoic acid hydrochloride (18)**: mp 231–233° dec; ir (KBr), 4.95 ($^+NH_3$), 5.91 (C=O) and 6.20 μ (NH); nmr (D_2O), δ 2.72 (s, 2, CH_2), 1.30 (s, 3, CH_3), and 0.93 [s, 9, $C(CH_3)_3$].

Anal. Calcd for $C_8H_{18}NO_2Cl$: C, 49.10; H, 9.27; N, 7.16. Found: C, 49.40; H, 9.45; N, 7.28.

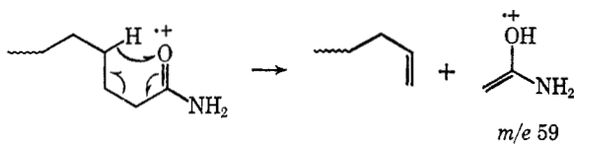
Preparation of 1,1,2,2-Tetramethylcyclopropane-3,3-d_2 (9-d_2).—To a stirred solution of 51 g (0.2 mol) of **24**[16] in 150 ml of ether under nitrogen at 0° was slowly added 73 g (3.1 g-atoms) of sodium in small pieces. Simultaneously, wet methanol-*d* (50 g of D_2O in 150 g of CH_3OD) was added dropwise. At the end of the reduction (2.5 hr), an additional 50 g of D_2O were added. The ether layer was separated and the aqueous layer was extracted with 50 ml of ether. The combined ether extracts were dried ($MgSO_4$) and distilled to give 3.7 g (18.5%) of **9**-d_2: bp 73–75°; ir (CCl_4), 4.31 and 4.50 μ (CD); nmr (neat), δ 1.08 (s, 12, CH_3).

Reaction of CSI with 9-d_2.—The same procedures used for the preparation and isolation of **10** and **11** from **9** converted **9**-d_2 into **10**-d_2 and **11**-d_2, mp 124–125°. Benzenethiol–pyridine reduction of **10**-d_2 gave **17**-d_2, mp 135–145°. Both **11**-d_2 and **17**-d_2 were spectroscopically and chromatographically pure.

Mass Spectral Analysis.—Table I summarizes the ion fragments in the mass spectra of undeuterated (**17**, **11**) and deuterated (**17**-d_2, **11**-d_2) β-lactam and unsaturated amide products. Worthy of note is that the base peak at *m/e* 84 in **17** is due to the loss of the *t*-butyl group. In **17**-d_2 the base peak remains at *m/e* 84 indicating the deuterium to be in the *t*-butyl moiety. Further, in **17**-d_2 there is a new peak 17 mass units below the molecular ion due to the loss of $-CHD_2$. The intensity ratio of the peaks at M − 15 and M − 17 in **17**-d_2 is 2.67:1. The predicted ratio would be 2:1 if loss of methyl came exclusively from the *t*-butyl group and 3:1 if loss of methyl from C-4 were also included. The virtual absence of a peak at M − 16 indicates that the deuterium is contained in just one methyl group and is not scrambled. Additional evidence for the presence of deuterium in the *t*-butyl group is seen by comparing the clusters of fragments in **17** at *m/e* 55 ($C_4H_7^+$) and 57 ($C_4H_9^+$) and at *m/e* 67 ($C_5H_7^+$), 69 ($C_5H_9^+$), and 71 ($C_5H_{11}^+$) with the corresponding clusters in **17**-d_2. The first cluster involves the *t*-butyl group while the second is composed of the moiety C-4 to C-9 as numbered in Table I.

In **11**, the base peak at *m/e* 83 results from cleavage between C-2 and C-3 followed by rearrangement to the more stable allylic ion. In **11**-d_2, the base peak is shifted to *m/e* 85 indicating the deuterium to be not at C-2 but somewhere further down the aliphatic chain. **11** shows a loss both of CH_3 $(M - 15)^+$ and NH_3 $(M - 17)^+$, while in **11**-d_2 the M − 17 peak is enhanced indicating loss of CHD_2 as well. In **11**, the intensity ratio of 124:126 is 1:16 while in **11**-d_2, the ratio of 126:128 falls to 1:2 which is the expected ratio if one of the three equivalent methyl groups is dideuterated. As in the case of **17**, additional support for the presence of deuterium in the *t*-butyl portion of the molecule is had by comparing the cluster of peaks at *m/e* 55 to 58 in **11** and **11**-d_2.

One final observation must include the *m/e* 59 peak of **11**. This is a typical amide rearrangement peak which arises as shown in eq 1. In the case of **11**, the only γ hydrogens available



m/e 59 (1)

for the six-membered cyclic transition state are the $=CH_2$ group. If there were only deuterium on this group, we should see only an *m/e* 60 in **11**-d_2. The six-membered transition state, however, is most probably *not* in effect here because it would call for the formation of a triple bond in the neutral leaving fragment which is in fact unknown to date. Seven-membered transition states are reported however;[18] thus, the rearrangement hydrogen in **11** comes from one of the methyls of the *t*-butyl group. That deuterium is present in the *t*-butyl moiety of **11**-d_2 becomes apparent with the observation that *m/e* 60 increases to about 25% of *m/e* 59 in **11**-d_2. This is roughly equivalent to the view that two of the nine equivalent δ hydrogens are, in fact, deuterium.

Isomerization of Cyclopropanes to Olefins.—In general, the cyclopropane (1 g) was stirred with 0.5 g of catalyst (H_3PO_4 or 20% Ac_2O in H_3PO_4) in a stoppered flask for 48 hr at room temp. The products were then analyzed by vpc. In each case, the major components were identified by (i) addition of authentic samples to the cyclopropane–olefin mixtures and observation of increase in peak heights and (ii) comparison of the retention times of each major component with those of authentic samples.

H_3PO_4.—Cyclopropane **1** gave a mixture of **1** (55%) and **5** (40%), while **6** led to a mixture of **6** (55%) and **8** (45%). In each isomerization, a third unidentified product was obtained in 5% yield.

Ac_2O–H_3PO_4.—Cyclopropane **1** gave a mixture of **1** (50%) and **5** (45%), while **6** led to a mixture of **6** (45%) and **8** (45%). In each instance, a third unidentified product (5–10%) was obtained.

The isomerization of **6** (1 g) was also effected by admixture with 0.5 g of analytically pure **7** in a stoppered flask and stirring for 1 week. Vpc then showed the presence of equal amounts of **6** and **8**, and less than 1% any other products.

Registry No.—**1**, 1630-94-0; **6**, 4127-45-1; **7**, 17060-95-6; **8**, 563-79-1; **9**, 4127-47-3; **9**-d_2, 17060-99-0; **10**, 17061-00-6; **11**, 17072-50-3; **11**-d_2, 17072-51-4; **12**, 594-56-9; **15**, 13423-22-8; **16**, 17072-53-6; **17**, 17061-02-8; **17**-d_2, 17061-03-9; **18**, 17072-54-7; chlorosulfonyl isocyanates, 1189-71-5.

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