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Effective Intramolecular Hydrogen Abstraction by the Sulfonamide Radical

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To study the reactivity of the sulfonamide radical in various reaction systems, the photodecomposition of *N*-*t*-butyl and *N*-methyl-*N*-chloroalkanesulfonamides was investigated. In benzene, the competitive hydrogen abstraction by the chlorine atom occurred to an appreciable extent and the participation of the chlorine atom was retarded with N_2-flow control. In an aqueous solution (AcOH-H_2O, *t*-BuOH-H_2O), the quantitative conversion to γ- and δ-chloroalkanesulfonamide was observed; this was thought to be due to the intramolecular hydrogen abstraction by the sulfonamide radical and to the lowering of the reactivity of the chlorine atom because of the solvation by H_2O. In an acid solution (AcOH-H_2O-H_2SO_4), a higher preference for 1,5 hydrogen transfer was found; this was caused by the protonated sulfonamide radical. The formation ratio of γ- to δ-chloroalkanesulfonamide in several solvents was determined, and the reactivity of the sulfonamide radical was discussed. From the reaction products obtained, several aliphatic sultams were synthesized.

In studies of the free-radical rearrangement of *N*-halo-compounds, the decompositions of *N*-haloamides,[1-4] *N*-haloimides,[5] and *N*-halosulfonamides[6-8] have been reported. These reactions have been reported to proceed in a manner similar to the Hofmann-Löffer reaction,[9] but the rearrangement of these compounds proceeds in the absence of an acid catalyst. It is interesting to study the properties of these nitrogen radicals because intermediates for five and six-membered-ring heterocycles syntheses can be obtained in the reaction of these compounds. In the hydrogen abstraction in these reactions described above, three processes can be assumed; intramolecular hydrogen abstraction by the nitrogen radical, intermolecular hydrogen abstraction by the nitrogen radical, and hydrogen abstraction by the halogen atom.

In previous papers[6] the present authors reported that *N*-alkyl-*N*-chloroalkanesulfonamides, especially *N*-*t*-butyl-*N*-chloroalkanesulfonamides, rearranged to the corresponding chloroalkanesulfonamides and that the reaction proceeded mainly *via* the intramolecular hydrogen abstraction by the sulfonamide radical; the participation of the chlorine atom in the hydrogen abstraction was thought to be relatively small in the decomposition of *N*-*t*-butyl-*N*-chloroalkanesulfonamides. However, in a further investigation of this reaction, the competitive hydrogen abstraction by the chlorine atom was observed to some extent in certain reaction systems, together with intramolecular hydrogen abstraction by the sulfonamide radical, and so a reinvestigation of the mechanism of the hydrogen transfer was necessary. Further, we found that the decomposition of *N*-halosulfonamides in the aqueous solution was a suitable method for effecting intramolecular hydrogen abstraction by the sulfonamide radical.

In the present paper, the properties of intramolecular hydrogen abstraction by the sulfonamide radical were studied in several reaction systems.

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2) A. L. J. Beckwith and J. E. Goodrich, *Aust. J. Chem.*, **18**, 747 (1965).

3) R. S. Neale, N. L. Marcus, and R. G. Schpers, *J. Amer. Chem. Soc.*, **88**, 3051 (1966).

4) Y. L. Chow and T. C. Joseph, *Chem. Commun.*, **1969**, 490.

5) R. C. Petterson and A. Wambsgans, *J. Amer. Chem. Soc.*, **86**, 1648 (1964).

6) a) M. Okahara, T. Ohashi, and S. Komori, *Tetrahedron Lett.*, **1967**, 1629. b) M. Okahara, T. Ohashi, and S. Komori, *J. Org. Chem.*, **33**, 3066 (1968).

7) T. Ohashi, M. Sugie, M. Okahara, and S. Komori, *Tetrahedron*, **25**, 5349 (1969).

8) R. S. Neale and N. L. Marcus, *J. Org. Chem.*, **34**, 1808 (1969).

9) M. E. Wolff, *Chem. Rev.*, **63**, 55 (1963).

TABLE 1. PHOTOREARRANGEMENT[a] OF *N*-*t*-BUTYL-*N*-CHLORO-*n*-HEXANESULFONAMIDE IN BENZENE OR AcOH

Solvent	N_2 flow rate ml/min	Concn. mol/*l*	Recovery rate[c] %	Composition of reaction product (wt%)		
				Original sulfonamide	*x*-Chlorohexane-sulfonamide[d]	Isomer ratio γ-Cl/δ-Cl/ε-Cl
Benzene	400	0.2	91	12.9	85.0	1.6/1.0/0.1
Benzene	150	0.2	90	22.2	75.1	1.3/1.0/0.5
Benzene	0	0.2	86	22.5	77.0	1.2/1.0/0.8
AcOH	150	0.2	80	38.5	60.0	1.2/1.0/0.6

a) Irradiation with a 150-W high pressure Hg lamp, 28—30°C under nitrogen unless specified otherwise.
b) Determined by glpc
c) The weight of the product obtained/the weight of *N*-chlorosulfonamide ×100.
d) *N*-*t*-Butyl-γ, δ and ε-chlorohexanesulfonamide.

TABLE 2. PHOTOREARRANGEMENT OF *N*-*t*-BUTYL-*N*-CHLORO-*n*-BUTANESULFONAMIDE IN BENZENE

Concn. mol/*l*	N_2 flow rate ml/min	Recovery rate %	Composition of reaction product (wt%)			
			Original sulfonamide	γ-Chlorobutane-sulfonamide	δ-Chlorobutane-sulfonamide	Isomer ratio γ-Cl/δ-Cl
0.4	400	93	16.8	71.1	11.3	6.29
0.4	150	92	22.7	62.5	13.3	4.70
0.4	40	90	35.3	52.5	12.2	4.30
0.4	0	90	33.4	53.3	13.0	4.10
Neat	150	90	35.1	51.3	13.2	3.89
0.4 in CCl_4	150	80	55.0	30.0	12.5	2.40

Results and Discussion

The Participation of the Chlorine Atom and the Effect of N_2-Flow Rate. To apply our results, reported in a previous paper[6] and shown in Scheme 1, the photodecomposition of *N*-*t*-butyl-*N*-chlorohexanesulfonamide was investigated in benzene in a manner similar to that described in the previous paper; the glpc analysis of the products showed the presence of ε-chlorohexanesulfonamide[10] together with γ- and δ-chlorohexanesulfonamides. The formation of ε-chlorohexanesulfonamide can not be explained by the intramolecular hydrogen abstraction; this shows the occurrence of hydrogen abstraction by the chlorine atom or intermolecular hydrogen abstraction by the sulfonamide radical.

Therefore, in order to study the competitive hydrogen abstraction by chlorine and sulfonamide radicals, a series of photodecompositions of *N*-*t*-butyl-*N*-chloroalkanesulfonamides (C_4–C_6) and *N*-chloro-*N*-methylbutanesulfonamide was investigated, and the isomer ratios of the chloroalkanesulfonamides were determined under various conditions.

$$RCH_2CH_2CH_2CH_2SO_2NClR' \xrightarrow[\text{in benzene}]{h\nu} \begin{cases} \rightarrow RCH_2CHClCH_2CH_2SO_2NHR' \\ \rightarrow RCHClCH_2CH_2CH_2SO_2NHR' \\ \rightarrow RCH_2CH_2CH_2CH_2SO_2NHR' \end{cases}$$

R=H, Me; R′=*t*-Bu, Me

Scheme 1

The results of the photodecomposition of *N*-*t*-butyl-*N*-chlorohexanesulfonamide in benzene are described in Table 1. As Table 1 shows, the formation of ε-chlorohexanesulfonamide varied with the N_2-flow rate; the isomer ratio of ε-chlorohexanesulfonamide decreased, and the yield[11] of *x*-chlorohexanesulfonamide increased, when the N_2-flow rate was high. These results suggest that chlorine participates in the hydrogen abstraction to an appreciable extent in benzene when the N_2-flow rate is low; *i. e.*, the hydrogen abstraction by the chlorine atom is retarded by the expulsion of chlorine and HCl with the N_2-flow control, and consequently the intramolecular hydrogen abstraction[12] by the sulfonamide radical proceeds mainly. Similar findings, that the yield of conversion and the isomer ratio vary with the N_2-flow rate, were observed in the photodecomposition of *N*-*t*-butyl-*N*-chlorobutanesulfonamide in benzene (Table 2). As is shown in Table 2, the value of the isomer ratio (γ-Cl/δ-Cl) obtained in the reaction in benzene is higher than that in CCl_4. This seems to show the difference in solvent effect on the chlorine atom between benzene and CCl_4.[13] In the decomposition of *N*-*t*-butyl-*N*-chlorobutanesulfonamide in benzene, the isomer ratio is larger than that in the reaction of *N*-*t*-butyl-*N*-chlorohexanesulfonamide, because δ-hydrogen of butanesulfonamide is primary.

It is important to determine whether *N*-*t*-butyl-δ-chlorobutanesulfonamide is formed as a result of hydrogen abstraction by the sulfonamide radical or by the chlorine atom. Neale[8] has recently reported that no

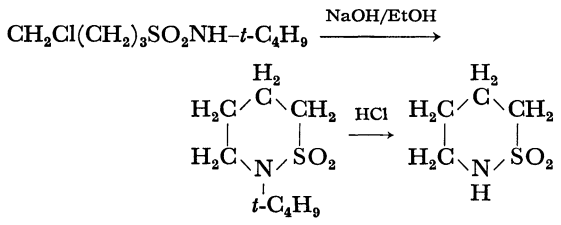
10) This was identified by comparing the gas chromatogram with that of the photochlorination product of *N*-*t*-butyl-*n*-hexanesulfonamide, and by the NMR of the reaction mixture, in which the doublet peak of methyl protons (τ, 8.46) was observed.

11) The yield of the conversion to *x*-chloroalkanesulfonamide was thought to be low because of the reaction of *N*-chloroalkanesulfonamide with HCl when the chlorine atom participates in the hydrogen abstraction.

12) The participation in the intermolecular hydrogen abstraction by the sulfonamide radical was thought to be small considering the fact that the yield of the conversion and the isomer ratio vary with the N_2-flow rate.

13) G. A. Russel, *J. Amer. Chem. Soc.*, **80**, 4987 (1958).

N-*t*-butyl-δ-halobutanesulfonamides were observed in the decomposition of *N*-chloro-and *N*-bromo-*N*-*t*-butylbutanesulfonamide. In our investigation, the results of the photodecomposition of *N*-bromo-*N*-*t*-butylbutanesulfonamide agreed with those of Neale, but an appreciable content of δ-chlorobutanesulfonamide was observed in the reaction of *N*-*t*-butyl-*N*-chlorobutanesulfonamide in benzene and CCl_4. The formation of *N*-*t*-butyl-δ-chlorobutanesulfonamide[14] was confirmed by the isolation of butanesultam by the alkali treatment of reaction products, followed by acidification with concentrated HCl, as is shown in Scheme 2.



Scheme 2

From these results, it may be concluded that, in the decomposition of *N*-chloroalkanesulfonamide in benzene and CCl_4, competitive hydrogen abstraction by the chlorine atom occurs and that this chlorine atom participation[15] can be somewhat retarded by the expulsion of chlorine and HCl by means of N_2-flow control, and that, in the decomposition of *N*-*t*-butyl-*N*-chlorobutanesulfonamide, the primary hydrogen abstraction by the sulfonamide radical does not occur and *N*-*t*-butyl-δ-chlorobutanesulfonamide is formed *via* hydrogen abstraction by the chlorine atom. This conclusion is supported by the fact that no δ-bromo isomer was observed in the decomposition of *N*-bromo-*N*-*t*-butylbutanesulfonamide; the hypothesis described in our previous paper[6] that *N*-*t*-butyl-δ-chlorobutanesulfonamide is formed by means of the primary hydrogen abstraction by the sulfonamide radical[16] *via* the seven-membered-ring transition state seems thus to be contradicted.

Effective Intramolecular Hydrogen Abstraction in the Aqueous Solution. To cause the selective rearrangement of *N*-chloroalkanesulfonamides, the participation of the chlorine atom must be suppressed; therefore, the photodecomposition of *N*-chloroalkanesulfonamides in aqueous solvents was investigated. Irradiation was carried out with a high-pressure Hg lamp at 28—30°C under N_2 until the active chlorine content was negligible. In every case, a complete loss of active chlorine was observed in 1 hr. The results obtained in aqueous AcOH are listed in Tables 3—6. In the photodecomposition of *N*-*t*-butyl-*N*-chlorobutanesulfonamide (Table 3), the yield of rearranged products and the isomer ratio (γ-Cl/δ-Cl) rose with an increase of the concentration of water, and in the solvents with higher water concentrations ($AcOH/H_2O=1.7$), *N*-*t*-butyl-γ-chlorobutanesulfonamide was obtained almost quantitatively and no δ-chlorobutanesulfonamide was observed. The fact that the formation of *N*-*t*-butyl-δ-chlorobutanesulfonamide is suppressed as well as the reaction of *N*-bromo-*N*-*t*-butylbutanesulfonamide in benzene suggests that a predominant intramolecular hydrogen transfer by the sulfonamide radical occurs and that the participation of the chlorine atom is retarded in the aqueous solution. Similar results were obtained in the reaction of *N*-*t*-butyl-*N*-chloropentane and hexanesulfonamides (Tables 4 and 5), and no appreciable content of ε-chlorohexanesulfonamide was observed in the decomposition of *N*-*t*-butyl-*N*-chlorohexanesulfonamide in a solution with a higher water concentration. This demonstrates the suppression of hydrogen abstraction by the chlorine atom and intermolecular hydrogen abstraction by the sulfonamide radical in the $AcOH-H_2O$ system.

The isomer ratio (γ-Cl/δ-Cl=1.93—1.94) observed in the reaction of *N*-*t*-butyl-*N*-chlorohexanesulfonamide in aqueous acetic acid ($AcOH/H_2O=2.5—2.1$) seems to show that the intramolecular 1,5 hydrogen transfer by the sulfonamide radical occurs in preference to the 1,6 hydrogen transfer because of a quasi-six-membered ring transition state.[18] The isomer ratio (γ-Cl/δ-Cl= 1.10—1.14) determined in the reaction of *N*-*t*-butyl-*N*-chloropentanesulfonamide in aqueous acetic acid is lower than that of *N*-*t*-butyl-*N*-chlorohexanesulfonamide. This result may be due to the stability of the δ-carbon radical resulting from the contribution of the hyperconjugation of the Me group.

This efficient solvent effect could be adapted to the decomposition of *N*-chloro-*N*-methyl-*n*-butanesulfonamide, which has been reprted to proceed less efficiently than the *N*-*t*-butyl analog.[6,8] As is shown in Table 6, *N*-methyl-γ-chlorobutanesulfonamide was obtained in a high yield; this is in accordance with the results obtained in the reaction of the *N*-*t*-butyl analog in the aqueous solution.

To compare the reactivity of the sulfonamide radical in the aqueous AcOH solution with that in a higher acidic solution, the photodecomposition of *N*-*t*-butyl-*N*-chloroalkanesulfonamides in the $AcOH-H_2O-H_2SO_4$ solvent was studied under the same conditions as were used in the $AcOH-H_2O$ system (Tables 3, 4, and 5). Although the conversion to *N*-*t*-butylchloroalkanesulfonamide was rather low because of the decomposition of the intermediate conjugate acid[6,19] to unsubstituted sulfonamides, the isomer ratio (γ-Cl/δ-Cl) was higher than that obtained in the $AcOH-H_2O$ system.

The relative greater facility of 1,5-shifting in H_2SO_4 may be due to the fact that the six-membered transition state is stereochemically more favorable for the protonated sulfonamide radical than for the neutral radical considering the steric repulsions involving non-bonded

14) The NMR of the viscous liquid obtained after the isolation of the γ-chloro isomer and *N*-*t*-butylbutanesulfonamide showed the presence of the δ-chloro isomer (τ, 6.45).

15) In benzene, the chlorine atom would act as the $C_6H_6Cl\cdot$ complex.

16) The absence of the δ-bromo isomer can not be explained by assuming intra- or intermolecular primary hydrogen abstraction by the sulfonamide radical. The high reactivity of the sulfonamide radical towards secondary hydrogens has previously been reported.[17]

17) A. E. Fuller and W. J. Hickinbottom, *J. Chem. Soc.*, **1965**, 3228.

18) Because of its low I strain of cyclohexane-like chair-formed conformation, the six-membered-ring transition state would be more stable than the seven-membered-ring transition state.

19) a) R. E. Buckles, *J. Amer. Chem. Soc.*, **71**, 1157 (1944). b) C. Derbyshire and W. A. Waters, *J. Chem. Soc.*, **1950**, 573.

Table 3. Photorearrangement[a] of *N*-*t*-butyl-*N*-chloro-*n*-butanesulfonamide in aqueous AcOH

Solvent[b]	Concn. mol/*l*	Recovery rate %	Composition of reaction product (wt%)			
			Original sulfonamide	γ-Chloro-butane-sulfonamide	δ-Chloro-butane-sulfonamide	Isomer ratio γ-Cl/δ-Cl
AcOH-H_2O (10.0/1.0)	0.4	85	40.0	50.6	8.3	6.10
AcOH-H_2O (3.4/1.0)	0.4	90	11.4	82.3	5.6	14.70
AcOH-H_2O (2.0/1.0)	0.4	94	2.0	91.0	6.0	15.17
AcOH-H_2O (1.7/1.0)	0.2	94	trace	99.0	trace	—
AcOH	0.4	88	29.0	56.7	14.9	3.80
AcOH-H_2O-H_2SO_4 (3.7/2.7/1.0)	0.4	65	48.4	51.3	trace	—

a) N_2 flow rate is 150 ml/min.
b) Values in parentheses are the volume ratio of AcOH to H_2O or H_2O–H_2SO_4.

Table 4. Photorearrangement[a] of *N*-*t*-butyl-*N*-chloro-*n*-pentanesulfonamide

Solvent	Concn. mol/*l*	Recovery rate %	Composition of reaction product (wt%)		
			Original sulfonamide	γ- and δ-Chloro-pentane-sulfonamide	Isomer ratio γ-Cl/δ-Cl
AcOH-H_2O (5.0/1.0)	0.1	90	15.0	83.0	1.10
AcOH-H_2O (2.0/1.0)	0.1	92	6.0	92.0	1.14
AcOH-H_2O-H_2SO_4 (12/4/1)	0.1	80	32.3	66.0	1.29
AcOH-H_2O-H_2SO_4 (7/3/1)	0.1	65	52.6	46.7	1.48
AcOH-H_2O-H_2SO_4 (8.4/5.9/1.0)[b]	0.16	82	32.1	67.7	1.50
AcOH	0.1	80	37.0	58.1	0.94
Benzene	0.1	87	23.0	72.0	0.95—1.00

a) N_2 flow rate is 150 ml/min.
b) This result is cited from the previous paper.[6]

Table 5. Photorearrangement[a] of *N*-*t*-butyl-*N*-chloro-*n*-hexanesulfonamide in aqueous solution

Solvent	Concn. mol/*l*	Recovery rate %	Composition of reaction product (wt%)		
			Original sulfonamide	γ- and δ-Chloro-hexanesulfon-amide	Isomer ratio γ-Cl/δ-Cl
AcOH-H_2O (7.0/1.0)	0.2	83	26.5	69.0[b]	1.70[c]
AcOH-H_2O (4.0/1.0)	0.4	90	10.0	88.5	1.80
AcOH-H_2O (3.0/1.0)	0.2	92	7.3	90.3	1.84
AcOH-H_2O (2.5/1.0)	0.2	92	6.5	92.5	1.93
AcOH-H_2O (2.1/1.0)	0.2	95	3.1	95.0	1.93
AcOH-H_2O (2.1/1.0)	0.1	94	1.4	96.5	1.94
t-BuOH-H_2O (1.0/1.0)	0.2	88	trace	98.6	1.89
AcOH-H_2O-H_2SO_4 (13/6/1)	0.1	87	17.0	82.3	2.30
AcOH-H_2O-H_2SO_4 (25/16/1)	0.1	85	22.2	76.0	2.10

a) N_2 flow rate is 150 ml/min.
b) The formation of ε-chlorohexanesulfonamide was observed. This value contains the quantity of ε-Cl isomer.
c) γ-Cl/δ-Cl/ε-Cl=1.70/1.00/0.50

Table 6. Photorearrangement[a] of *N*-chloro-*N*-methyl-*n*-butanesulfonamide in aqueous AcOH

Solvent	Concn. mol/*l*	Recovery rate %	Composition of reaction product (wt%)			
			Original sulfonamide	γ-Chloro-butane-sulfonamide	δ-Chloro-butane-sulfonamide	Isomer ratio γ-Cl/δ-Cl
AcOH-H_2O (1.75/1.00)	0.15	89	6.4	89.7	1.0	89.7
AcOH-H_2O (1.40/1.00)	0.15	90	2.5	94.1	trace	—

a) N_2 flow rate is 150 ml/min.

Table 7. UV Spectrum of *N*-chlorosulfonamides

RSO_2NCl-*t*-C_4H_9	Solvent[a)]	Max. mμ (ε)
R=C_5H_{11}	Benzene	276 (178)
R=C_5H_{11}	AcOH	269 (115)
R=C_5H_{11}	AcOH-H_2O (7:4)	267 (89)
R=C_6H_{13}	Benzene	279 (172)
R=C_6H_{13}	AcOH-H_2O-H_2SO_4 (3:1:1)	244 (52)

a) Values in parentheses are the volume ratio of AcOH, H_2O, and H_2SO_4.

atoms in the transition state; this is analogous with the case of the aminium radical[20] in the Hofmann-Löffler reaction.

From the result that selective 1,5 and 1,6 hydrogen transfers do not occur in pure AcOH (Table 1), it is clear that the presence of water promotes the intramolecular hydrogen abstraction by the sulfonamide radical; the same result was obtained in the photodecomposition of *N*-*t*-butyl-*N*-chlorohexanesulfonamide in aqueous *t*-BuOH (Table 5).

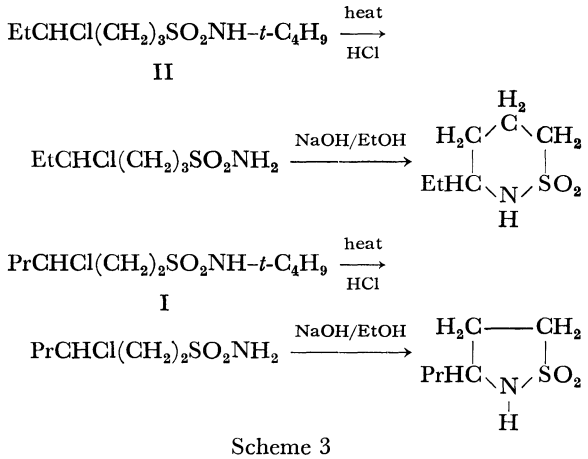
From the UV spectrum of *N*-chlorosulfonamides, *N*-chlorosulfonamide is evidently protonated in a H_2SO_4 solution, but the absorption in aqueous AcOH is not as characteristic as that in pure AcOH (Table 7).

From these results, it may be considered that the sulfonamide radical is not protonated in aqueous AcOH, but that the reactivity of the chlorine atom is lowered as a result of the solvation by H_2O, and that, consequently, the intramolecular hydrogen abstraction by the sulfonamide radical proceeds predominantly.

Although the solvation of the sulfonamide radical and the solvation of the transition state for rearrangement may be assumed, the evidence is not conclusive at present. From this point of view, the decomposition of *N*-bromoalkanesulfonamides, in which the participation of the halogen atom seems to be small, is under investigation.[21]

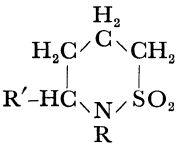
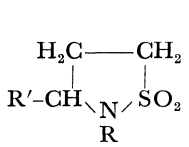
Aliphatic Sultams. In a previous paper,[6] we have reported the conversion of *N*-*t*-butyl-γ-chloropentanesulfonamide to *N*-*t*-butyl-3-ethylpropanesultam. In a similar manner, *N*-*t*-butyl-3-methylpropanesultam and *N*-*t*-butylbutanesultam were obtained almost quantitatively from *N*-*t*-butyl-γ-chloro and *N*-*t*-butyl-δ-chlorobutanesulfonamides respectively by the treatment of the rearranged products with ethanolic NaOH. Neale[8] has reported the formation of *N*-*t*-butyl-2-methylcyclopropanesulfonamide, together with *N*-*t*-butyl-3-methylpropanesultam, by various alkali treatments of *N*-*t*-butyl-γ-halobutanesulfonamide, but no evidence of the formation of significant amounts of the cyclopropane isomer was observed upon treatment with ethanolic NaOH, and *N*-*t*-butyl-3-methylpropanesultam was isolated almost quantitatively by distillation. The structure of this sultam was confirmed by NMR and mass spectra. On the other hand, the analogous treatment of *N*-*t*-butyl-δ-chloropentanesulfonamide with ethanolic NaOH gave *N*-*t*-butylpent-3-enesulfonamide almost quantitatively. This suggests that the formation of six-membered-ring sultams containing the *N*-*t*-butyl group and a side chain at the 4-position does not proceed so efficiently as the formation of five-membered-ring sultams and that, consequently, the elimination reaction occurs predominantly. The formation of 4-methylbutanesultam in a high yield from δ-chloropentanesulfonamide demonstrates the lack of a stereochemical barrier of the *N*-*t*-butyl group.

N-*t*-Butyl-γ-chloro (I) and *N*-*t*-butyl-δ-chlorohexanesulfonamides (II) were identified by the fact that 3-propylpropanesultam and 4-ethylbutanesultam were obtained by the alkali treatment of chlorohexanesulfonamides derived by the treatment of I and II with HCl as is shown in Scheme 3:



Scheme 3

Table 8. Mass spectrum[a)] of aliphatic sultams

		*m/e*
R′=Et, R=H		163 (M^+), 162 (M^+-H), 134 (M^+-Et), 70 (M^+-Et-SO_2)
	R′=Pr, R=H	163 (M^+), 162 (M^+-H), 120 (M^+-Pr), 56 (M^+-Pr-SO_2)
R′=H, R=H		135 (M^+), 134 (M^+-H), 107 (M^+-C_2H_4), 70 (M^+-H-SO_2)
R′=Me, R=H		149 (M^+), 148 (M^+-H), 134 (M^+-Me), 121 (M^+-C_2H_4), 70 (M^+-Me-SO_2)
R′=H, R=*t*-C_4H_9		191 (M^+), 176 (M^+-Me), 136 (M^+-Me-C_3H_4), 112 (M^+-Me-SO_2)
	R′=Me, R=*t*-C_4H_9	191 (M^+), 176 (M^+-Me), 136 (M^+-Me-C_3H_4), 120 (136-CH_4), 112 (176-SO_2)

a) 70 eV.

20) E. J. Corey and W. R. Hertler, *J. Amer. Chem. Soc.*, **82**, 1657 (1960).

21) In contribution, T. Ohashi, M. Okahara, and S. Komori, This Bulletin, **44**, (1971), in prss.

The structure of each five- and six-membered-ring sultam was confirmed by a study of its mass spectrum (Table 8).

Experimental

Apparatus. The IR spectra were run on an IR-E-type Nihon Bunko spectrometer. The NMR spectra were obtained with a Japan Electron Optics Lab. spectrometer (JNM3H-60). The UV spectra were taken on an EPS-3 Hitachi recording spectrometer. The glpc analyses were conducted by a Shimadzu GC-3A apparatus using Apieson L grease 10%, Silicone DC 200 10%, or Silicone oil 550 10% on Diasolid L; 60—80 mesh; 1 m column. The mercury lamp used was an Eikosha 150-W high-pressure mercury lamp.

Materials. The benzene, AcOH, and CCl_4 were purified by an ordinary method.

Titrations for active Cl were conducted by an $Na_2S_2O_3$ assay of the I_2 liberated from 10% aqueous KI acidified with 0.1N HCl.

Preparation of N-*Halo*-N-*alkyl*-n-*alkanesulfonamides.* *N-t*-Butyl-*N*-chlorobutane, pentanesulfonamides, and *N*-chloro-*N*-methylbutanesulfonamide were prepared as has been described in a previous paper.[6] The *N*-chlorination of *N-t*-butyl-*n*-hexanesulfonamide was done in the same manner, and the *N-t*-butyl-*N*-chlorohexanesulfonamide obtained quantitatively was purified by distillation. Bp 113—115°C/0.2 mmHg, n_D^{20} 1.4730. IR: 2960, 1350, 1150, and 890 cm^{-1}.

Found: Cl, 13.6%. Calcd for $C_{10}H_{22}ClNO_2S$: Cl, 13.86%.

N-*Bromo*-N-t-*butyl*-n-*butanesulfonamide.* *N-t*-Butyl-*n*-butanesulfonamide (0.05 mol) was suspened in water (100 ml) in the presence of Na_2CO_3 (21 g); bromine (32 g) was added to the stirred suspension at 10°C, and the solution was stirred for 4 hr. The insoluble oil separated as a lower layer was collected and dissolved in CCl_4. The solution was dried over anhydrous Na_2SO_4, and the solvent was evaporated. Yield, 75%, IR: 2960, 1340, 1145, and 890 cm^{-1}. n_D^{20} 1.4955.

Found: Br, 29.1%. Calcd for $C_8H_{18}BrNO_2S$: Br, 29.36%.

Photodecomposition of N-*Halosulfonamides.* *N*-Alkyl-*N*-halo-*n*-alkanesulfonamides were irradiated at 28—30°C under N_2 with a high-pressure mercury lamp inside a reaction flask until the active halogen content of the solution was negligible. All the reactions were completed in 1 hr. In the reaction in benzene, reaction products were obtained after the evaporation of the benzene, while in the reaction in aqueous solvents the reaction mixture was poured onto ice and the organic layer was extracted with ether.

Isolation and Analyses of Reaction Products. Analyses of the reaction products obtained in the reaction of *N-t*-butyl-*N*-chloro-*n*-butane and pentanesulfonamides were carried out as has been described in a previous paper.[6]

N-t-*Butyl*-n-*hexanesulfonamide.* This was isolated by distillation from the reaction products obtained in the reaction of *N-t*-butyl-*N*-chlorohexanesulfonamide. Bp 118°C/0.2 mmHg. IR: 3280, 2960, 1320, and 1140 cm^{-1}.

Found: C, 54.26; H, 10.45: N, 6.21%. Calcd for $C_{10}H_{23}NO_2S$: C, 54.26; H, 10.47; N, 6.33%.

N-t-*Butyl-γ-chloro- and δ-chlorohexanesulfonamides.* On the cooling of the hexane solution of the products obtained in the photorearrangement of *N-t*-butyl-*N*-chlorohexanesulfonamide in an AcOH-H_2O solvent to −40°C, a white precipitate was obtained. This precipitate melted at room temperature; glpc and elemental analysis showed it to be a mixture of the two rearranged products. On the cooling of an ether solution of this mixture, *N-t*-butyl-*δ*-chlorohexanesulfonamide was isolated as a white precipitate; it was then recrystallized from ether and hexane. Mp 58°C. IR: 3280, 2960, 1320, and 1130 cm^{-1}. NMR (in $CDCl_3$): τ; 5.45 (1H), 6.10 (multiplet, 1H), 6.80 (triplet, 2H), 7.70—8.55 (multiplet, 6H), 8.65 (singlet, 9H), 8.95 (triplet, 3H).

Found: C, 46.89; H, 8.64; N, 5.40; Cl, 13.6%. Calcd for $C_{10}H_{22}ClNO_2S$: C, 46.95: H, 8.67; N, 5.43; Cl, 13.86%.

The isolation of another rearranged product, *N-t*-butyl-*γ*-chlorohexanesulfonamide, was tried, but it was unsuccessful because of contamination by a small amount of the *δ*-chloro isomer.

N-*Methyl-γ-chlorobutanesulfonamide.* The liquid obtained from the decomposition of *N*-chloro-*N*-methylbutanesulfonamide in AcOH-H_2O (0.15 mol/*l*, 20 min irradiation) was distilled under reduced pressure. Bp 133°C/0.1 mmHg, n_D^{25} 1.4765. IR: 3300, 2960, 1320, 1140, and 850 cm^{-1}. NMR (in $CDCl_3$): τ; 5.40 (1H), 5.85 (multiplet, 1H), 6.80 (triplet, 2H), 7.20 (doublet, 3H), 7.80 (multiplet, 2H), 8.43 (doublet, 3H).

Found: C, 32.00; H, 6.53; N, 7.49; Cl, 18.8%. Calcd for $C_5H_{12}ClNO_2S$: C, 32.35; H, 6.52; N, 7.55; Cl, 19.09%.

N-t-*Butyl-γ-bromobutanesulfonamide.* The irradiation of a benzene solution of *N*-bromo-*N-t*-butyl-*n*-butanesulfonamide (0.4 mol/*l*) with a high-pressure mercury lamp produced a viscous liquid (recovery rate, 91%) which was found by glpc to contain 25.0% of *N-t*-butyl-*n*-butanesulfonamide and 74.2% of *N-t*-butyl-*γ*-bromobutanesulfonamide; no formation of the *δ*-bromo isomer was observed. A white precipitate obtained by adding hexane to the reaction mixture was recrystallized from cold ether. Mp 69°C. IR: 3300, 1310, 1130, and 1000 cm^{-1}. NMR (in $CDCl_3$): τ; 5.40 (1H), 5.80 (multiplet, 1H), 6.80 (triplet, 2H), 7.75 (multiplet, 2H), 8.25 (doublet, 3H), 8.63 (singlet, 9H).

Found: C, 35.55; H, 6.94; N, 5.13; Br, 29.2%. Calcd for $C_8H_{18}BrNO_2S$: C, 35.30; H, 6.66; N, 5.15; Br, 29.36%.

Preparation of Sultams. N-t-*Butyl*-3-*methylpropanesultam*: To 50 ml of the EtOH solution of *N-t*-butyl-*γ*-chlorobutanesulfonamide[6] (0.01 mol), 0.013 mol of NaOH was added; the solution was then refluxed for 3 hr. The solution was cooled and carefully neutralized with conc. HCl. The salt was filtered off; the residue obtained after the evaporation of EtOH was almost pure, and its IR showed the disappearance of the NH band. It was purified by distillation at reduced pressure. Bp 96—97°C/0.5 mmHg, n_D^{20} 1.4780 (lit,[8] n_D^{25} 1.4733). Yield, 97%. IR: 2960, 1300, 1130, 1020, 980, and 950 cm^{-1}. NMR (in $CDCl_3$): τ; 6.20 (multiplet, 1H), 6.65—7.10 (multiplet, 2H), 7.20—8.30 (multiplet, 2H), 8.60—8.68 (singlet and doublet, 12H).

Found: C, 50.03; H, 9.01%. Calcd for $C_8H_{17}NO_2S$: C, 50.23; H, 8.96%.

N-t-*Butyl-butanesultam*: *N-t*-Butyl-*δ*-chlorobutanesulfonamide[6] (0.01 mol) was dissolved in EtOH (50 ml). NaOH (0.013 mol) was added, and the solution was refluxed for 3 hr. The salt thus formed was filtered off, and the solvents was evaporated. The residue was extracted with ether (50 ml); a white precipitate, which was obtained by adding hexane to the cold ether solution, was then recrystallized from ether and hexane; mp 43°C; yield, 94%. IR: 2960, 1325, 1140, 1020, 920, and 880 cm^{-1}. NMR (in $CDCl_3$): τ; 6.55 (triplet, 2H), 7.00 (triplet, 2H), 7.80 (multiplet, 2H), 8.30 (multiplet, 2H), 8.55 (singlet, 9H).

Found: N, 7.06%. Calcd for $C_8H_{17}NO_2S$: N, 7.33%.

Butanesultam: The reaction mixture (2.8 g) consisting 40% of *N-t*-butyl-*δ*-chlorobutanesulfonamide obtained after the isolation of *N-t*-butyl-*γ*-chlorobutanesulfonamide from the reaction products of *N-t*-butyl-*N*-chlorobutanesulfonamide was treated with ethanolic NaOH (0.5 g) as has been described above and then acidified with conc. HCl. The residue

obtained after the removal of the salt was dissolved in $CHCl_3$ and ether; then hexane was added and cooled. A white precipitate which separated out (0.6 g) was recrystallized from $CHCl_3$ and ether. The same compound was obtained quantitatively by the treatment of *N-t*-butylbutanesultam with conc. HCl in EtOH at room temperature. Mp 115°C (lit.[22] 114—115°C). IR: 3240, 2960, 1320, 1130, 1030, 955, and 770 cm^{-1}. NMR (in $CDCl_3$): τ; 5.70 (1H), 6.60 (multiplet, 2H), 6.90 (triplet, 2H), 7.81 (multiplet, 2H), 8.37 (multiplet, 2H).

Found: C, 35.28; H, 6.83; N, 10.26%. Calcd for $C_4H_9NO_2S$: C, 35.54; H, 6.71; N, 10.36%.

N-t-*Butylpent-3-enesulfonamide*: *N-t*-Butyl-δ-chloropentanesulfonamide[6] (0.01 mol) was dissolved in 50 m*l* of EtOH and then treated with NaOH (0.013 mol) in a manner similar to that described in the synthesis of *N-t*-butyl-3-methylpropanesultam. When the liquid thus obtained was distilled, the corresponding sultam was not obtained, but *N-t*-butylpent-3-enesulfonamide was obtained; bp 120—122°C/1mmHg, n_D^{20} 1.4680; yield, 92%. IR: 3300, 2960, 1320, 1130, and 1000 cm^{-1}. NMR (in $CDCl_3$): τ; 4.57 (multiplet, 2H), 5.40 (1H), 6.90 (triplet, 2H), 7.53 (multiplet, 2H), 8.35 (doublet, 3H), 8.62 (singlet, 9H).

Found: C, 52.31; H, 9.31%. Calcd for $C_9H_{19}NO_2S$: C, 52.65; H, 9.33%.

4-Methylbutanesultam: *N-t*-Butyl-δ-chloropentanesulfonamide (2.4 g) was heated in 40 m*l* of the HCl solution (HCl : H_2O= 3 : 1, ratio of volume) at 90°C for 6 hr. The viscous liquid (1.8 g) obtained after the evaporation of the water was washed with cold hexane and treated with NaOH (0.4 g) in 50 m*l* of EtOH under reflux for 2 hr and then neutralized with HCl. A white precipitate (1.3 g) was obtained by the treatment described in the isolation of butanesultam and was recrystallized from $CHCl_3$ and ether; mp 112°C; yield, 87%. IR: 3280, 2960, 1310, 1130, 950, and 780 cm^{-1}. NMR (in $CDCl_3$): τ; 5.60 (1H), 6.50 (multiplet, 1H), 6.93 (multiplet, 2H), 7.70—8.50 (multiplet, 4H), 8.78 (doublet, 3H).

Found: C, 39.88; H, 7.38; N, 9.33%. Calcd for $C_5H_{11}NO_2S$: C, 40.25; H, 7.43; N, 9.38%.

4-Ethylbutanesultam: *N-t*-Butyl-δ-chlorohexanesulfonamide (2.6 g) was heated in 40 m*l* of a HCl solution in the same manner as has been described in the preparation of 4-methylbutanesultam. The viscous liquid (1.9 g) thus obtained was treated with NaOH (0.4 g) in 50 m*l* of EtOH. A white precipitate (1.4 g) was obtained by the treatment described above and recrystallized from $CHCl_3$ and ether; mp 106°C; yield, 84%. IR: 3230, 2960, 1320, 1130, and 780 cm^{-1}. NMR (in $CDCl_3$): τ; 5.85 (1H), 6.50—7.10 (multiplet, 3H), 7.80 (multiplet, 2H), 8.50 (multiplet, 4H), 9.03 (triplet, 3H).

Found: C, 43.95; H, 7.95; N, 8.33%. Calcd for $C_6H_{13}NO_2S$: C, 44.15; H, 8.02; N, 8.58%.

3-Propylpropanesultam: A mixture (2.6 g) consisting 90% of *N-t*-butyl-γ-chlorohexanesulfonamide and 10% of *N-t*-butyl-δ-chlorohexanesulfonamide was treated with HCl; a white crystal (1.7 g) isolated from the semisolid liquid obtained after the cleavage of the *t*-butyl bond was submitted to the alkali treatment, and the liquid (1.1 g) thus obtained was purified by distillation; bp 115°C/0.1 mmHg; yield, 80%. IR: 3220, 1320, 1130, and 830 cm^{-1}. NMR (in $CCCl_4$): τ; 5.00 (1H), 6.50 (multiplet, 1H), 6.95 (multiplet, 2H), 7.50—8.70 (multiplet, 6H), 9.05 (triplet, 3H).

Found: C, 43.78; H, 7.89; N, 8.49%. Calcd for $C_6H_{13}NO_2S$: C, 44.15; H, 8.02; N, 8.58%.

22) H. Feichtinger, *Chem. Ber.*, **96**, 3068 (1963).