Solvolysis of *cis*-2-Hydroxycyclohexylcarbinyl Brosylate.—A solution of 3.52 g of the hydroxy brosylate, prepared as previously described, 100 ml of acetone, 83 ml of 1.26 *M* phosphate buffer (pH 6.8), and 60 ml of water was refluxed for 151 hr. The reaction mixture was processed in the usual manner and glpc on a 5 ft × 0.25 in. column packed with 20% Carbowax 20M on firebrick gave three products (in order of elution): 2-methylcyclohexanone (17%) identified by comparison with an authentic sample, *cis*-2-hydroxymethyl cyclohexanol (76%), and *trans*-2-hydroxy-1-methylcyclohexanol (7%) identified by comparison with an authentic sample, mp 78–80° (lit.[33] mp 85°), prepared as previously described.[33] A component of shorter retention time than 2-methylcyclohexanone was found to be formed from acetone when exposed to the reaction solvent in the absence of the hydroxy brosylate.

Solvolysis of 2-Methyl-2-hydroxymethylpropyl Tosylate.—A mixture of 1.95 g of the tosylate and 50 ml of 0.4 *M* acetate buffer (pH 4) was heated in a sealed tube at 115° for 72 hr. The mixture was continuously extracted with ether and the ether was distilled under a factionating column. The residue was found to contain 95% 2-methylbutanal and 5% 2,2-dimethyl-1,3-propanediol by glpc using a 5 ft × 0.25 in. column packed with 5% SE 30 on Chromosorb W at 120°. An alliquot of the reaction mixture was treated with 2,4-dinitrophenylhydrazine solution to afford 2-methylbutanal 2,4-dinitrophenylhydrazone, mp 125–126° (lit.[34] mp 120°). The yield corresponded to 32% based on starting arenesulfonate. Another experiment afforded 2-methylbutanal 2,4-dinitrophenylhydrazone in 36% yield. A weighed sample of pure 2-methylbutanal gave the 2,3-dinitrophenylhydrazone in 36% yield.

(33) S. Nametkin and A. Jarzeff, *Ber.*, **56**, 1803 (1923).

Registry No.—(−)-*trans*-2-hydroxymethylcyclohexyl brosylate, 16897-79-3; *cis*-2-hydroxymethylcyclopentanol, 1883-85-8; *trans*-2-carbomethoxycyclopentyl β-naphthalenesulfonate, 16897-81-7; *trans*-2-acetoxymethylcyclopentyl β-naphthalenesulfonate, 16897-82-8; *erythro*-2-methyl-1,3-butanediol, 16897-83-9; cyclopentanone ketal of *erythro*-2-methyl-1,3-butanediol, 16897-84-0; *threo*-2-methyl-1,3-butanediol, 16897-85-1; cyclopentanone ketal of *threo*-2-methyl-1,3-butanediol, 16897-86-2; tiglyl benzyl ether, 16897-87-3; (−)-*threo*-methyl-3-hydroxybutyl benzyl ether, 16897-88-4; 2-hydroxy-2-methyl-1-butyl benzyl ether, 16897-89-5; β-naphthalenesulfonate of *threo*-2-methyl-3-hydroxybutyl benzyl ether, 16897-90-8.

(34) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., p 320.

Synthesis of γ- and δ-Chloroalkanesulfonamides *via* the Photorearrangement of N-Chlorosulfonamides

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The photorearrangement of N-*t*-butyl- and N-methyl-N-chloroalkanesulfonamide in benzene and in acid solution was studied with the object of preparing γ- and δ-chloroalkanesulfonamides, intermediates for sultam synthesis. In benzene, γ- and δ-chloroalkanesulfonamides were formed almost exclusively from N-*t*-butyl derivatives, while, in the reaction of N-methyl-N-chlorobutanesulfonamide, β-chlorobutanesulfonamide was apparently formed in addition to γ- and δ-chlorobutanesulfonamides. In acid solution (H_2SO_4–AcOH), on the other hand, the rate of formation of γ-chloro derivatives increased and that of β-chloro derivatives decreased owing to the relatively higher reactivity of the protonated sulfonamide radical for intramolecular hydrogen abstraction. The isolation of each rearranged product from the reactions was undertaken and N-*t*-butyl-γ-chlorobutanesulfonamide N-*t*-butyl-δ-chloropentanesulfonamide, and N-*t*-butyl-γ-chloropentanesulfonamide were obtained pure.

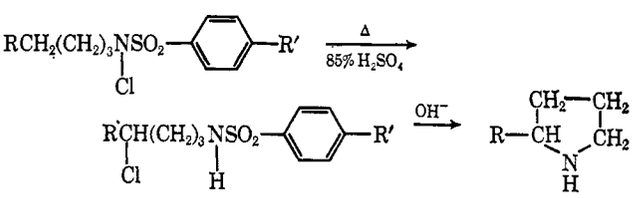
In studies on the free-radical rearrangement of N-halo compounds, the synthesis of pyrrolidine derivatives from N-haloamines (Hofmann–Löffler reaction[1]) and γ-lactone formation from N-haloamides[2–5] and N-haloimides[6] have been reported.

Although N-alkyl-N-chloroarylsulfonamides are reported to rearrange to N-δ-chloroalkyl derivatives[7] under similar reaction conditions as the Hofmann–Löffler reaction (Scheme I), the analogous rearrangement of N-alkyl-N-chloroalkanesulfonamides has not yet been reported.

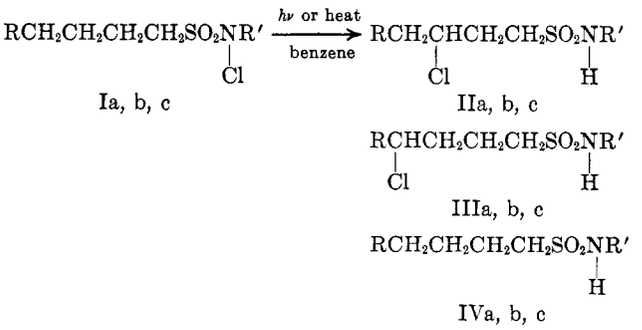
In a previous paper,[8] the authors reported that N-alkyl-N-chloroalkanesulfonamides readily rearrange to the corresponding chloroalkanesulfonamides under the influence of photoirradiation or heat (Scheme II).

The purpose of the present study was to investigate

SCHEME I



SCHEME II



a, R = H; R′ = *t*-C_4H_9
b, R = H; R′ = CH_3
c, R = CH_3; R′ = *t*-C_4H_9

(1) M. E. Wolff, *Chem. Rev.*, **63**, 55 (1963).
(2) D. H. R. Barton and A. L. J. Beckwith, *Proc. Chem. Soc.*, 335 (1963).
(3) D. H. R. Barton, A. L. J. Beckwith, and A. Goosen, *J. Chem. Soc.*, 181 (1965).
(4) A. L. J. Beckwith and J. E. Goodrich, *Aust. J. Chem.*, **18**, 747 (1965).
(5) R. S. Neale, N. L. Marcus, and R. G. Schepers, *J. Amer. Chem. Soc.*, **88**, 3051 (1966).
(6) R. C. Petterson and A. Wambsgans, *ibid.*, **86**, 1648 (1964).
(7) G. H. Coleman, *Proc. Iowa Acad. Sci.*, **46**, 217 (1939).
(8) M. Okahara, T. Ohashi, and S. Komori, *Tetrahedron Lett.*, 1629 (1967).

TABLE I

PROPERTIES AND ANALYSES OF N-CHLOROSULFONAMIDES

Cl | RSO_2NR'	Bp, °C (mm)	$n^{20}D$	Ir absorptions, cm^{-1}	Uv absorptions[a] max, mμ (ε)	Cl, %[b,c]
R = *n*-C_4H_9; R′ = *t*-C_4H_9	86–87 (0.2)	1.4718	2960, 1360, 1155, 625, 587	274 (150)	15.3 (15.56)
R = *n*-C_4H_9; R′ = CH_3	99–100 (4)	1.4690	2960, 1350, 1150, 615, 570	265 (106)	18.9 (19.09)
R = *n*-C_5H_{11}; R′ = *t*-C_4H_9	110 (2)	1.4727	2960, 1345, 1150, 620, 570	275 (182)	14.4 (14.24)

[a] In ethanol. [b] Positive chlorine. [c] Values in parentheses are calculated values.

TABLE II

PHOTOREARRANGEMENT OF N-CHLOROSULFONAMIDES IN BENZENE[a]

Cl | RSO_2NR'	Concn, mol/l.	Reaction time, min	Recovery rate,[b] %	Reaction product: Cl, %	Original sulfonamide,[c] %	γ-Chloroalkanesulfonamide,[c] %	δ-Chloroalkanesulfonamide,[c] %
R = *n*-C_4H_9; R′ = *t*-C_4H_9	0.20	25	90	12.3	24.0	60.2	14.0
R = *n*-C_4H_9; R′ = *t*-C_4H_9	0.26	30	91	12.1	26.0	60.9	12.1
R = *n*-C_4H_9; R′ = *t*-C_4H_9	0.52	30	90	13.0	19.7	61.9	15.1
R = *n*-C_4H_9; R′ = *t*-C_4H_9	1.03	25	93	14.0	14.6	67.1	17.2
R = *n*-C_4H_9; R′ = *t*-C_4H_9	1.94	25	91	14.1	17.7	62.0	15.9
R = *n*-C_4H_9; R′ = *t*-C_4H_9	2.58	25	92	13.6	18.6	60.5	15.5
R = *n*-C_4H_9; R′ = *t*-C_4H_9	Neat	30	91	14.0	20.1	50.8	14.1
R = *n*-C_4H_9; R′ = CH_3[d-f]	0.27	35	85	8.8	48.6	20.3	0.5
R = *n*-C_5H_{11}; R′ = *t*-C_4H_9	0.85	20	93	13.1	19.9	42.1	38.0
R = *n*-C_5H_{11}; R′ = *t*-C_4H_9[g]	0.85	120	92	11.8	23.0	40.3	37.1

[a] Irradiation with a 150-W high pressure mercury lamp, 10–15°, under nitrogen unless specified otherwise. [b] The weight of the product obtained/the weight of N-chlorosulfonamides × 100. [c] Weight percent based on recovered reaction product, average values. [d] A compound (13.2%) thought to be β-chloro derivative was present in the reaction mixture in addition to those listed. [e] Very small amount of crystal identified as chlorinated benzene was isolated from the reaction mixture. [f] Average molecular weight of the reaction mixture, 192. [g] Irradiation with a 30-W low pressure mercury lamp, 10–13°, under nitrogen.

more fully the synthetic aspects of this new rearrangement.

Results and Discussion

The starting materials, N-*t*-butyl- and N-methyl-N-chloro-*n*-butanesulfonamide and N-*t*-butyl-N-chloro-*n*-pentanesulfonamide, were prepared by chlorinating the corresponding sulfonamides by the procedures previously described.[8]

These N-chlorosulfonamides are stable and can be purified by distillation at reduced pressure; their properties and chlorine content are shown in Table I.

The N-chlorosulfonamides were irradiated in benzene or acid solution at 10–15° under nitrogen with a high or low pressure mercury arc lamp equipped with a quartz filter until the positive chlorine content of the solution was negligible. Positive chlorine disappeared within 35 min in benzene solution, whereas in acid solution the reaction needed a longer time. The reaction product from benzene solution was recovered almost quantitatively after the removal of the solvent; it was analyzed by glpc.

Glpc analysis of the products generally showed three major peaks. One peak was identified as the original sulfonamide (IVa, b) and, from N-*t*-butyl- or N-methyl-N-chloro-*n*-butanesulfonamide, two other peaks were identified as N-alkyl-γ-chlorobutanesulfonamide (IIa, b) and N-alkyl-δ-chlorobutanesulfonamide (IIIa, b), respectively, by means of a comparison of their retention times with those of the authentic compounds.

However, in the gas chromatogram of the product from N-chloro-N-methyl-*n*-butanesulfonamide, the peak of δ-chlorobutanesulfonamide was very small, and another peak was observed preceding the peak of IIb. This peak was supposed to correspond to N-methyl-β-chlorobutanesulfonamide (VIII) by comparing the gas chromatogram with that of the photochlorination product of N-methyl-*n*-butanesulfonamide.[9]

In the case of N-*t*-butyl-N-chloro-*n*-pentanesulfonamide, two peaks in the gas chromatogram were also identified as N-*t*-butyl-γ- and -δ-chloropentanesulfonamide, respectively, by nmr analysis of the isolated products, and the peaks corresponding to the other isomers, that is β- or ε-chloropentanesulfonamide, were not observed. Quantitative analysis of the rearranged products was also done by glpc. Results of the reaction in benzene are shown in Table II.

In the reaction of N-*t*-butyl-N-chloro-*n*-butanesulfonamide, not much difference was observed in the composition of the products over the concentration range 0.20–2.58 mol/l.

Formation of products of higher molecular weight was suggested in the irradiation of N-chloro-N-methyl-*n*-butanesulfonamide because the total amount of each compound, determined by glpc, was rather low (about 83%) and the average molecular weight of the reaction mixture was slightly higher than the calculated value. Intramolecular dehydrochlorination is presumed to occur competitively in this case, where hydrogens are present on the carbon atom adjacent to nitrogen, as observed by Neale[5] in the rearrangement of N-halo-N-methylamides.

When the reaction was carried out in acid solution (H_2O–H_2SO_4–AcOH), the recovery rate of the product decreased slightly, and the amount of unsubstituted

(9) Although this compound could not be isolated in the pure state, it was ascertained to contain one bound chlorine atom in the molecule. Also, in photochlorination of many aliphatic compounds,[10-12] it is known that the retention times of the position isomers increase in order of the increase of the position number of chlorine, that is, 1 < 2 < 3 . . . .

(10) L. Horner and L. Schlafer, *Ann. Chem.*, **635**, 31 (1960).

(11) H. Singh and J. M. Tedder, *J. Chem. Soc., Sect. B*, 608 (1966).

(12) M. Okahara, S. Yanagida, and S. Komori, *Tech. Rept. Osaka Univ.*, **17**, 205 (1967).

TABLE III

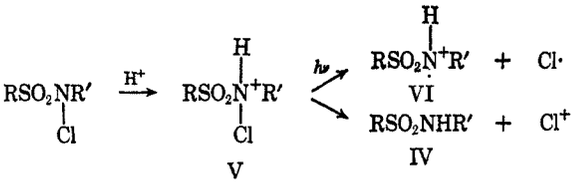
PHOTOREARRANGEMENT OF N-CHLOROSULFONAMIDE IN H_2O–H_2SO_4–AcOH

RSO_2NR' (Cl on N)	Reaction time, min	Recovery rate, %	Reaction product: Cl, %	Unsubstituted sulfonamide, wt %[a]	γ-Chloroalkanesulfonamide, wt %[a]	δ-Chloroalkanesulfonamide, wt %[a]
R = *n*-C_4H_9; R′ = CH_3[b-d]	240	70	9.6	47.9	36.8	0.5
R = *n*-C_5H_{11}; R′ = *t*-C_4H_9[b,e]	90	75	10.1	32.4	43.6	24.0
R = *n*-C_5H_{11}; R′ = *t*-C_4H_9[f,e]	50	78	10.8	28.9	43.1	27.6
R = *n*-C_5H_{11}; R′ = *t*-C_4H_9[f,g]	45	82	10.3	32.1	40.6	27.1

[a] Weight percent based on recovered reaction products, average value. [b] Irradiation with a low pressure mercury arc lamp (30 W) inside the reaction vessel. [c] Ten grams of sample dissolved in 140 g of acid solution (a mixture of 11.2 g of H_2SO_4, 50.6 g of H_2O, and 78.2 g of AcOH). [d] A compound (7.0%) thought to be N-methyl-N-β-chlorobutanesulfonamide was found in the reaction product in addition to the compounds listed. [e] The sample (2.3 g) dissolved in 40 g of acid solution (H_2SO_4, 4.8 g; AcOH, 13.5 g; H_2O, 21.7 g). [f] Irradiation with a high pressure mercury arc lamp (150 W) inside the reaction vessel. [g] Ten grams of sample dissolved in 264 g of acid solution (H_2SO_4, 30.6 g; AcOH, 139.6 g; H_2O, 93.8 g).

original sulfonamides increased, but the formation of γ-chloroalkanesulfonamide was greatly raised as shown in Table III.

The higher ratio of formation of γ- to δ-chloroalkanesulfonamide in acid solution is assumed to be due to the relatively higher reactivity of intramolecular hydrogen abstraction by the protonated sulfonamide radical (VI) in the competition between intra- and intermolecular hydrogen abstraction. However, the decomposition of the intermediate conjugate acid (V) to unsubstituted sulfonamides (IV), as reported by Buckles,[13] and Derbyshire[14] with N-bromoamides and N-bromosuccinimides, would occur to a certain extent.



At the step of hydrogen abstraction, three processes are supposed to occur competitively, *i.e.*, the intramolecular hydrogen abstraction by sulfonamide radical (process 1), the intermolecular hydrogen abstraction by sulfonamide radical (process 2), and the hydrogen abstraction by chlorine atom (process 3).

In the decomposition of N-*t*-butyl-N-chloro-*n*-alkanesulfonamides in benzene, process 1 is the main process but process 2 would participate competitively to an appreciable extent in the reaction. On the other hand, in the decomposition of N-chloro-N-methyl-*n*-butanesulfonamide in benzene, process 3 is supposed to be the main process because the distribution of products is similar to that obtained in the photochlorination of N-methyl-*n*-butanesulfonamide in benzene.

In the decomposition of N-*t*-butyl-N-chloro-*n*-pentanesulfonamide in acid solution, the higher formation ratio of γ- to δ-chloro derivative strongly suggests that process 1 is the main process and process 2 is retarded owing to the solvation and the electrostatic repulsion between the positively charged species.[15]

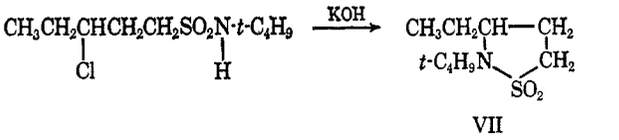
Furthermore in the decomposition of N-chloro-N-methyl-*n*-butanesulfonamide in acid solution, perhaps the three processes competitively occur. However, processes 2 and 3 are supposed to be suppressed to some extent because the formation of a compound thought to be β-chloro derivative was found to be small.

Isolation of the rearranged products from the reaction mixture was also undertaken. Unsubstituted sulfonamides could be separated by distillation under reduced pressure. N-*t*-butyl-γ-chlorobutanesulfonamide (IIa) was isolated as a white crystalline solid from the reaction product of N-*t*-butyl-N-chloro-*n*-butanesulfonamide (Ia) by adding petroleum ether, but isolation of N-*t*-butyl-δ-chlorobutanesulfonamide (IIIa) in the pure state was unsuccessful because its content was generally small.

On the other hand, analogous treatment of the reaction product from N-*t*-butyl-N-chloro-*n*-pentanesulfonamide (Ic) afforded a pure compound as a white crystalline solid, corresponding to the peak having a longer retention time in the gas chromatogram. This compound was confirmed to be N-*t*-butyl-δ-chloropentanesulfonamide (IIIc) because the nmr signal of the terminal methyl protons (τ 8.50) was a doublet.

From the filtrate obtained after removing N-*t*-butyl-δ-chloropentanesulfonamide, a white crystal was isolated by column chromatography on active alumina. This compound was confirmed to be N-*t*-butyl-γ-chloropentanesulfonamide (IIc) because, in its nmr spectrum, the terminal methyl protons (τ 8.93) was a triplet and the methylene protons (τ 6.72) adjacent to N-*t*-butylsulfonamide group was a triplet.

Furthermore a five-membered-ring sultam, N-*t*-butyl-3-ethylpropane sultam (VII), was isolated from the reaction mixture obtained by the alkali treatment of the irradiation product of N-*t*-butyl-N-chloro-*n*-pentanesulfonamide.



VII

The structure of this five-membered-ring sultam was confirmed by its nmr spectrum in which the absorption (τ 9.10) of the terminal methyl protons in the side-chain ethyl group was found to be split into a triplet.

(13) R. E. Buckles, *J. Amer. Chem. Soc.*, **71**, 1157 (1944).

(14) C. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 573 (1950).

(15) Also, a referee has pointed out that a six-membered transition state is stereochemically more favorable for the protonated N radical than for the neutral radical.

Experimental Section[16]

N-*t*-Butyl-*n*-butanesulfonamide.—*n*-Butanesulfonyl chloride (78.4 g, 0.5 mol), prepared as described by Douglass and Johnson,[17] was added to an ether solution (200 ml) of *t*-butylamine (95.2 g, 1.3 mol) with stirring at 5° over 1 hr. After removal of precipitated *t*-butylamine hydrochloride, the ether solution was washed with water and dried over anhydrous sodium sulfate. The residue, obtained by evaporation, was distilled under reduced pressure to yield N-*t*-butyl-*n*-butanesulfonamide [72.4 g (75%)]: bp 155–156° (6 mm); n^{20}D 1.4530. Characteristic infrared bands appeared at 3280, 2960, 1320, 1140, and 1000 cm^{-1}.

Anal. Calcd for $C_8H_{19}NO_2S$: C, 49.69; H, 9.93; N, 7.25. Found: C, 49.68; H, 9.95; N, 7.12.

N-Methyl-*n*-butanesulfonamide.—As described above, *n*-butanesulfonyl chloride (78.4 g, 0.5 mol) was allowed to react with a 30% aqueous solution of methylamine (130 g) yielding N-methyl-*n*-butanesulfonamide (60.4 g, 80%): bp 147–148° (4 mm); n^{20}D 1.4528. Characteristic infrared bands appeared at 3300, 2960, 1320, and 1140 cm^{-1}.

Anal. Calcd for $C_5H_{13}NO_2S$: C, 39.70; H, 8.68; N, 9.26. Found: C, 39.65; H, 8.50; N, 9.35.

N-*t*-Butyl-*n*-pentanesulfonamide.—Reaction of *n*-pentanesulfonyl chloride (50 g) with *t*-butylamine (48.2 g) in ether (200 ml) afforded N-*t*-butyl-*n*-pentanesulfonamide (49.7 g, 83%): bp 125–126 (2 mm); n^{20}D 1.4531. Characteristic infrared bands appeared at 3280, 2960, 1450, 1320, and 1130 cm^{-1}.

Anal. Calcd for $C_9H_{21}NO_2S$: C, 52.15; H, 10.21; N, 6.76. Found: C, 52.02; H, 10.23; N, 6.56.

N-Chlorination of N-Alkylalkanesulfonamides.—N-Alkyl-*n*-alkanesulfonamide (0.1 mol) was suspended in water (150 ml) in the presence of sodium hydroxide (4 g). Chlorine gas was passed into the stirred suspension at 5–10° until the yellow color of chlorine persisted. The insoluble yellow oil that separated as a lower layer was washed with water and dried over anhydrous sodium sulfate. The colorless liquid obtained in quantitative yield was almost pure and could be further purified by distillation at reduced pressure. The properties of N-chloro-N-alkyl-*n*-alkanesulfonamides are described in Table I.

The Photorearrangement of N-*t*-Butyl-N-chloro-*n*-butanesulfonamide in Benzene.—N-*t*-Butyl-N-chloro-*n*-butanesulfonamide (10 g) in anhydrous benzene (85 ml) was irradiated at 10–15° under nitrogen with a high pressure mercury arc lamp inside the reaction flask until the active chlorine content of the solution was negligible. After evaporation of the solvent, a pale yellow viscous liquid (9.3 g) was obtained. This product contained three main compounds, as shown by glpc analysis on a column of 10% Apiezon L grease or silicone grease DC 200 on Diasolid L (60–80 mesh, 1 m, column temperature 210°, hydrogen carrier gas, 150 cc/min). Components were identified as IVa, IIa, and IIIa, in order of increasing retention time, by comparison of their retention times with those of the pure compounds. Quantitative analysis was done by glpc using N-methyl-*n*-propanesulfonamide as an internal standard. Results of the reaction at various concentrations are shown in Table II.

The Photorearrangement of N-*t*-Butyl-N-chloro-*n*-pentanesulfonamide in Benzene.—Irradiation of N-*t*-butyl-N-chloro-*n*-pentanesulfonamide (35 g) in anhydrous benzene (180 ml) with a high pressure mercury arc lamp produced a yellow viscous liquid (32.6 g) which was found to contain only three compounds, identified as IVc (19.9%), IIc (42.1%), and IIIc (38.0%). The similar result was obtained in the decomposition reaction using a low pressure mercury arc lamp (Table II). Glpc was on a column of Triton X-305 10% on Diasolid L (60–80 mesh, 1 m, column temperature, 170°, hydrogen carrier gas, 150 cc/min).

The Photorearrangement of N-Chloro-N-methyl-*n*-butanesulfonamide in Benzene.—Irradiation of N-chloro-N-methyl-*n*-butanesulfonamide (10 g) in anhydrous benzene (200 ml) produced a pale yellow liquid (8.5 g; Cl, 8.8%). This was analyzed by glpc on a column of Triton X-305 10% on Diasolid L (60–80 mesh, 1 m, column temperature, 174°, hydrogen carrier gas, 115 cc/min). It contained IVb (48.6%), IIb (20.3%), VIII (13.2%), and IIIb (0.5%).

A small amount (about 70 mg) of white crystals (mp 153°) also separated from the reaction products. By ir and elemental analysis, it was identified as chlorinated benzene.

Anal. Calcd for $C_6H_6Cl_6$: C, 24.78; H, 2.08. Found: C, 25.02; H, 2.49.

The Photochlorination of N-Methyl-*n*-butanesulfonamide.—N-methyl-*n*-butanesulfonamide (6 g) was dissolved in benzene (120 ml), and chlorine gas was passed into the solution at 10–13° under irradiation with a high pressure mercury arc lamp. The yellow viscous liquid obtained after removing benzene (Cl, 3.8%) was analyzed by glpc and found to contain IVb (78.3%), IIb (8.8%), IIIb (trace), a compound assumed to be N-methyl-β-chlorobutanesulfonamide (VIII) (6.2%), and the chlorinated benzene.

Photorearrangement of N-Chloro-N-methyl-*n*-butanesulfonamide and N-*t*-Butyl-N-chloro-*n*-pentanesulfonamide in Acid Solution.—N-Chloro-N-methyl-*n*-butanesulfonamide (10.0 g) in acid solution (11.2 g of H_2SO_4, 50.6 g of H_2O, 78.2 g of AcOH) was irradiated with a low pressure mercury arc lamp (30 W) at 10–15° under nitrogen until the active chlorine was negligible. The reaction mixture was poured onto ice, and the organic layer was extracted with ether. The pale yellow liquid obtained (7.0 g; Cl, 9.6%) was analyzed by glpc and found to contain IVb (47.9%), IIb (36.8%), VIII (7.0%), and a trace amount of IIIb. N-*t*-Butyl-N-chloro-*n*-pentanesulfonamide (2.3 g) was also irradiated in an analogous manner in acid solution (4.8 g of H_2SO_4, 13.5 g of AcOH, and 21.7 g of H_2O). The yellow liquid obtained (1.7 g; Cl, 10.1%) was found to contain IVc (32.4%), IIc (43.6%), and IIIc (24.0%) by glpc using a Triton-X column. Similar results were obtained in the decomposition using a high pressure, mercury arc lamp (Table III).

Preparation of Authentic Compounds. N-*t*-Butyl-δ-chlorobutanesulfonamide.—4-Chlorobutanesulfonyl chloride [57 g, 0.3 mol; bp 108° (0.8 mm), lit.[18] bp 110–112° (1–1.5 mm)] was prepared from 4-chlorobutyl acetate as described by Helfreich.[18] It was added with stirring to an ethereal solution of *t*-butylamine (44 g, 0.6 mol) at 5°. After removing *t*-butylamine hydrochloride, the ether was evaporated, leaving white crystalline N-*t*-butyl-δ-chlorobutanesulfonamide. This was recrystallized from a small amount of ether: yield, 47.7 g (70%); mp 39.5°; nmr (in $CDCl_3$), τ 5.58 (singlet, 1 H), 6.45 (triplet, 2 H), 6.95 (triplet, 2 H), 8.05 (quintet, 4 H), and 8.61 (singlet, 9 H).

Anal. Calcd for $C_8H_{18}ClNO_2S$: C, 42.18; H, 7.98; N, 6.15; Cl, 15.56. Found: C, 42.05; H, 8.01; N, 6.30; Cl, 15.3.

N-*t*-Butyl-γ-chlorobutanesulfonamide.—3-Chlorobutanesulfonyl chloride was prepared by passing chlorine in the presence of water into α-acetyl-γ-chlorobutyl mercaptan (16.6 g), which was prepared by the addition of thiolacetic acid to 3-chloro-1-butene [bp 64–66° (760 mm), lit.[19] bp 63° (748 mm)], with rapid stirring at 5° until the aqueous layer became yellow. The yellow oil that separated was extracted with ether, washed with water, and dried over anhydrous sodium sulfate. Distillation of the residue obtained by evaporation of the ether afforded 3-chlorobutanesulfonyl chloride: yield, 11.2 g (62%); bp 95–97° (6 mm). 3-Chlorobutanesulfonyl chloride (19.1 g, 0.1 mol) was added to an ether solution (100 ml) of *t*-butylamine (14.6 g, 0.2 mol) with stirring at 5° over 1 hr. After removing *t*-butylamine hydrochloride and ether, white crystals were obtained. The product was recrystallized from a small amount of ether: yield, 15.9 g (70%); mp 63.0°; nmr (in $CDCl_3$), τ 5.30 (singlet, 1 H), 5.90 (multiplet, 1 H), 6.75 (triplet, 2 H), 7.80 (multiplet, 2 H), 8.42 (doublet, 3 H), 8.60 (singlet, 9 H).

Anal. Calcd for $C_8H_{18}ClNO_2S$: C, 42.18; H, 7.98; N, 6.15; Cl, 15.56. Found: C, 42.30; H, 8.18; N, 6.30; Cl, 15.7.

N-Methyl-δ-chlorobutanesulfonamide.—4-Chlorobutanesulfonyl chloride (19 g) was added with stirring to an aqueous solution (23 g) of methylamine at 5°. The yellow oil that separated was extracted with dichloromethane, washed with water, and dried over anhydrous sodium sulfate. Distillation of the residue obtained by evaporation of the solvent afforded N-methyl-δ-chlorobutanesulfonamide (12.9 g): bp 140–142° (0.2 mm); nmr in $CDCl_3$ τ 5.40 (1 H), 6.45 (triplet, 2 H), 6.93 (triplet, 2 H), 7.20 (doublet, 3 H), 8.08 (quintet, 4 H).

(16) Infrared spectra (KBr disks or liquid films) were recorded on a Nihon Bunko instrument; nmr spectra were obtained in CCl_4 or $CDCl_3$ solution. Glpc analyses were conducted using Apiezon L grease 10%, silicone DC 200 10%, or Triton X-305 10% on Diasolid L, 60–80 mesh, 4.5 mm × 1 m column. Titrations for positive chlorine were conducted by sodium thiosulfate assay of iodine liberated from 10% aqueous KI acidified with 0.1 *N* hydrochloric acid. Petroleum ether had bp 40–60°. The commercial, pure grade of benzene was dried over sodium wire and used as the reaction solvent.

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Anal. Calcd for $C_5H_{12}ClNO_2S$: C, 32.35; H, 6.52; Cl, 19.09. Found: C, 32.30; H, 6.31; Cl, 19.3.

N-Methyl-γ-chlorobutanesulfonamide.—3-Chlorobutanesulfonyl chloride (19.1 g, 0.1 mol) was added with stirring to a 30% aqueous solution of methylamine (24 g) at 5°. The yellow oil that separated was treated as described for N-methyl-δ-chlorobutanesulfonamide. Distillation of the residue obtained by evaporation of the solvent afforded N-methyl-γ-chlorobutanesulfonamide (11.1 g): bp 134–135° (0.1 mm); nmr in $CDCl_3$ τ 5.45 (singlet, 1 H), 5.85 (multiplet, 1 H), 6.80 (triplet, 2 H), 7.20 (doublet, 3 H), 7.80 (multiplet, 2 H), 8.43 (doublet, 3 H).

Anal. Calcd for $C_5H_{12}ClNO_2S$: C, 32.35; H, 6.52; Cl, 19.09. Found: C, 32.15; H, 6.41; Cl, 18.8.

Isolation of the Rearranged Products from the Reaction Mixture. Isolation of N-*t*-Butyl-*n*-butanesulfonamide.—The viscous liquid obtained in the photorearrangement was distilled under reduced pressure and a fraction of bp 120–122° (2 mm) was obtained. The ir and nmr spectra of this fraction were the same as those of known N-*t*-butyl-*n*-butanesulfonamide.

Isolation of N-*t*-Butyl-γ-chlorobutanesulfonamide.—A white precipitate was obtained when petroleum ether was added to the viscous liquid (9.0 g) obtained in the photorearrangement. The precipitate was collected by filtration and washed with cold light petroleum ether and then recrystallized from petroleum ether solution (yield 3.8 g), mp 63.0°, not depressed by mixture with the authentic compound. The ir and nmr spectra of this compound were the same as those of authentic N-*t*-butyl-γ-chlorobutanesulfonamide.

Isolation of pure N-*t*-butyl-δ-chlorobutanesulfonamide was unsuccessful because of its low initial content and the small difference in solubility in petroleum ether between γ- and δ-chlorobutanesulfonamides.

Isolation of N-*t*-Butyl-δ-chloropentanesulfonamide.—By adding petroleum ether to the reaction product (32.6 g; Cl ,13.1%) obtained from N-*t*-butyl-N-chloro-*n*-pentanesulfonamide (35.0 g), a white precipitate was obtained. This precipitate was collected by filtration, washed with cold petroleum ether, and recrystallized from petroleum ether. The white crystals (11 g), mp 59°, were identified as N-*t*-butyl-δ-chloropentanesulfonamide (IIIc) by the infrared and nmr spectra and elemental analysis. Characteristic infrared bands appeared at 3380, 2960, 1320, 1140, and 1020 cm^{-1}; nmr (in CCl_4) bands were at τ 4.70 (1 H), 6.00 (multiplet 1 H), 6.90 (triplet, 2 H), 8.15 (multiplet, 4 H), 8.50 (doublet, 3 H), and 8.60 (singlet, 9 H).

Anal. Calcd for $C_9H_{20}ClNO_2S$: C, 44.71; H, 8.34; Cl, 14.24. Found: C, 44.36; H, 8.36; Cl, 14.5.

Isolation of N-*t*-Butyl-γ-chloropentanesulfonamide.—The filtrate (10.0 g) obtained by the treatment described above was passed through an active alumina column and eluted with carbon tetrachloride. N-*t*-Butyl-γ-chloropentanesulfonamide (3.0 g) was isolated as a white crystal and purified by recrystallization from the petroleum ether solution, mp 42°. Characteristic infrared bands appeared at 3380, 2960, 1320, and 1140 cm^{-1}; nmr (in $CDCl_3$) bands were at τ 5.70 (1 H), 6.00 (multiplet, 1 H), 6.72 (triplet, 2 H), 7.83 (multiplet, 2 H), 8.30 (multiplet, 2 H), 8.60 (singlet, 9 H), 8.93 (triplet, 3 H).

Anal. Calcd for $C_9H_{20}ClNO_2S$: C, 44.71; H, 8.34; N, 5.79; Cl, 14.24. Found: C, 44.52; H, 8.51; N, 5.68; Cl, 14.3.

Isolation of N-*t*-Butyl-3-ethylpropanesultam.—The viscous liquid (24 g) obtained in the photoirradiation of N-chloro-N-*t*-butyl-*n*-pentanesulfonamide was dissolved in ethanol. Potassium hydroxide (6 g) was added, and the solution was refluxed for 3 hr. The salt that formed was filtered off, and the ethanol was evaporated. The residue (19 g) was dissolved in ether (50 ml), and the ether solution was extracted with water (50 ml). After evaporation of water, a yellow liquid (2 g) was obtained from the aqueous layer. This product was found to be almost pure by glpc, but it was further refined on a silica gel column. Characteristic infrared bands appeared at 2960, 1300, 1220, and 1135 cm^{-1}; nmr (in $CDCl_3$) bands were at τ 6.60 (multiplet, 1 H), 6.90 (triplet, 2 H), 7.80 (multiplet, 2 H), 8.40 (multiplet, 2 H), 8.60 (singlet, 9 H), and 9.10 (triplet, 3 H).

Anal. Calcd for $C_9H_{19}NO_2S$: C, 52.66; H, 9.33. Found: C, 53.06; H, 9.63.

Registry No.—Ia, 16339-81-4; Ib, 16867-16-6; Ic, 16867-17-7; IIa, 16339-82-5; IIb, 16867-19-9; IIc, 16867-20-2; IIIa, 16339-83-6; IIIb, 16867-22-4; IIIc, 16867-23-5; IVa, 16867-24-6; IVb, 16867-25-7; IVc, 16867-26-8; VII, 16867-27-9.

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Steric Enhancement of Resonance. IV. Absorption Spectra of N-Alkyl- and N,N-Dialkylpicramides

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Spectral displacements on N-alkylation and N,N-dialkylation of picramide are discussed in terms of inductive and steric effects. The phenomenon, *steric enhancement of resonance*, is considered to operate in this series.

In earlier papers of this series, it was proposed that an effect, characterized as *steric enhancement of resonance*, might explain progressive bathochromic displacements of ultraviolet maxima and longer wavelength band edges with increasing bulk of the substituent group in the 1-alkyl-2,4-dinitrobenzenes,[1] 1-alkyl-2,4,6-trinitrobenzenes,[2] and N,N-dialkyl-2,4-dinitroanilines.[3] We wish now to suggest that the same phenomenon accounts for spectral shifts in the N-alkyl- and N,N-dialkylpicramides, and discuss some aspects of conformation which may be deduced from the spectra.

The ultraviolet spectrum of picramide (1) in methanol shows two N→V bands above 250 mμ (Table I and Figure 1). From comparison with 2-nitro-, 4-nitro-, 2,4-dinitro- and 2,6-dinitroaniline spectra,[3] the max-

TABLE I

SPECTRA OF PICRAMIDE DERIVATIVES IN METHANOL[a]

		$(R_2{}^+N{=}C_1{\rightarrow}C_4{=}NO_2{}^-)$ transition			$(R_2{}^+N{=}C_1{\rightarrow}C_2{=}NO_2{}^-)$ transition		
	Picramide	λ_{max}, mμ	ν_{max}, cm^{-1}	ϵ_{max}	λ_{max}, mμ	ν_{max}, cm^{-1}	ϵ_{max}
1.	Unsubstituted	318	31,450	12,000	407	24,570	7,900
2.	N-Methyl-	337	29,670	14,700	408	24,510	6,290
3.	N-Ethyl-	338	29,590	14,960	410	24,390	6,120
4.	N-Isopropyl-	337.5	29,630	14,330	410	24,390	5,610
5.	N,N-Dimethyl-	(335)	(29,850)	(9,400)			
		371	26,950	11,670			
6.	N,N-Diethyl-	(335)	(29,850)	(6,750)			
		384	26,040	10,200			

[a] Values in parentheses are for shoulders or inflections.

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