BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1141—1143(1971)

The Photodecomposition of *N*-Bromosulfonamides

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(Received August 18, 1970)

In a previous paper,[1] the present authors reported a competitive hydrogen abstraction by the chlorine atom and the sulfonamide radical, and the predominant intramolecular hydrogen abstraction by the sulfonamide radical in an aqueous solution in the photodecomposition of *N*-alkyl-*N*-chloroalkanesulfonamides. It has also been reported[1,2] that *N*-*t*-butyl-*γ*-bromo-*n*-butanesulfonamide was formed in the photodecomposition of *N*-bromo-*N*-*t*-butyl-*n*-butanesulfonamide, unlike the result[1] obtained in the photodecomposition of *N*-*t*-butyl-*N*-chloro-*n*-butanesulfonamide. In this experiment, the photodecomposition of *N*-alkyl-*N*-bromo-*n*-alkanesulfonamides was investigated in order to study hydrogen abstraction by the sulfonamide radical.

N-Alkyl-*N*-bromo-*n*-alkanesulfonamides were prepared by the treatment of *N*-alkyl-*n*-alkanesulfonamides with freshly-prepared NaOBr in a buffer solution (Table 1). The results of the photodecomposition of *N*-bromosulfonamides are listed in Table 2. In the reaction of *N*-bromo-*N*-*t*-butyl-*n*-hexanesulfonamide in benzene, glpc and NMR analyses showed the formation of *N*-*t*-butyl-*γ*-bromo- (I) and *N*-*t*-butyl-*δ*-bromohexanesulfonamide (II), while the *ε*-bromo isomer was not formed. This suggests that the *γ*-and *δ*-bromo isomers were formed *via* intramolecular 1,5 and 1,6 hydrogen transfer by the sulfonamide radical, and that no intermolecular hydrogen abstraction by the sulfonamide radical or the bromine atom occurs; this is distinct from the result[1] observed in the reaction of *N*-*t*-butyl-*N*-chloro-*n*-hexanesulfonamide, in which the participation of the chlorine atom was observed. This must be due to the difference in reactivity between bromine and chlorine.

The isomer ratio (I/II=1.96—1.98) in this reaction was similar to that (*N*-*t*-butyl-*γ*-chlorohexanesulfonamide/*N*-*t*-butyl-*δ*-chlorohexanesulfonamide=1.93—1.94) observed in the reaction of *N*-*t*-butyl-*N*-chloro-*n*-hexanesulfonamide in an aqueous solution (AcOH/H_2O=2.1)[1]; a similar value (I/II=2.04) was obtained in the reaction of *N*-bromo-*N*-*t*-butyl-*n*-hexanesulfonamide in the AcOH–H_2O system. These facts support the hypothesis described in the previous paper[1] that the reactivity of the chlorine atom is retarded by solvation, that the predominant intramolecular hydrogen abstraction by the sulfonamide radical occurs in an aqueous solution, and that the reactivity in the hydrogen abstraction of the sulfonamide radical in the aqueous solution does not differ from that of the sulfonamide radical in benzene. The same result was obtained in the reaction of *N*-bromo-*N*-*t*-butyl-*n*-pentanesulfon-

TABLE 1. PROPERTIES AND ANALYSES OF *N*-BROMOSULFONAMIDES

RSO_2NBrR'	n_D	IR, cm^{-1}	UV[a] λ_{max}, nm(ε)	Br, %[b]
R=*n*-C_3H_7 R'=*t*-C_4H_9	1.4910[c]	2960, 1350, 1150, 890	315 (148)	30.7 (30.95)
R=*n*-C_4H_9 R'=*t*-C_4H_9	1.4955[d]	2960, 1340, 1145, 890	317 (149)	29.2 (29.36)
R=*n*-C_4H_9 R'=Me	1.5047[d]	2960, 1340, 1150, 790	310 (136)	34.5 (34.72)
R=*n*-C_5H_{11} R'=*t*-C_4H_9	1.4950[c]	2960, 1340, 1145, 890	318 (131)	27.6 (27.91)
R=*n*-C_6H_{13} R'=*t*-C_4H_9	1.5030[c]	2960, 1340, 1150, 890	320 (115)	26.5 (26.61)

a) In cyclohexane.
b) Values in parentheses are calculated values.
c) n_D^{32} d) n_D^{20}

1) T. Ohashi, S. Takeda, M. Okahara, and S. Komori, This Bulletin, **44**, 771 (1971).

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

Table 2. Photodecomposition of *N*-bromosulfonamides[a)]

RSO_2NBrR'	Concn. mol/*l*	React. time, min	Recovery rate,[c)] %	Composition[b)] of reaction product			
				I %	II %	III %	Isomer ratio, II/III
$R=n\text{-}C_6H_{13}$ $R'=t\text{-}C_4H_9$	0.2 in benzene	35	95	16.4	55.3	28.2	1.96
$R=n\text{-}C_6H_{13}$ $R'=t\text{-}C_4H_9$	0.4 in benzene	30	92	22.8	50.5	25.5	1.98
$R=n\text{-}C_5H_{11}$ $R'=t\text{-}C_4H_9$	0.2 in benzene	30	96	7.0	50.0	42.1	1.19
$R=n\text{-}C_4H_9$ $R'=t\text{-}C_4H_9$	0.2 in benzene	25	94	20.0	79.3	—	—
$R=n\text{-}C_4H_9$ $R'=t\text{-}C_4H_9$	0.2 in CCl_4	40	94	17.3	82.1	—	—
$R=n\text{-}C_4H_9$ $R'=t\text{-}C_4H_9$	0.2 in t-BuOH-H_2O[d)]	120	82	35.7	64.0	—	—
$R=n\text{-}C_3H_7$ $R'=t\text{-}C_4H_9$	0.2 in benzene	20	92	28.0	72.5	—	—
$R=n\text{-}C_6H_{13}$ $R'=t\text{-}C_4H_9$	0.2 in AcOH-H_2O[e)]	180	71	57.1	28.4	13.9	2.04
$R=n\text{-}C_4H_9$ $R'=Me$	0.2 in benzene	40	78	58.3	28.1[f)]	—	—

a) N_2 flow rate is 150ml/min.
b) Determined by glpc (wt %).
c) (The weight of the product obtained/the weight of *N*-bromosulfonamide) × 100
d) t-BuOH/H_2O=1.7 (volume ratio)
e) AcOH/H_2O=2.1 (volume ratio)
f) In addition to the compounds listed, the high molecular weight of product was observed (*m/e*=320).
I=RSO_2NHR', II=*N*-Alkyl-γ-bromo-*n*-alkanesulfonamide, III=*N*-Alkyl-δ-bromo-*n*-alkanesulfonamide

amide. The isomer ratio of the two rearranged products (γ-bromo isomer/δ-bromo isomer=1.19) was similar to that (*N*-*t*-butyl-γ-chloropentanesulfonamide/*N*-*t*-butyl-δ-chloropentanesulfonamide=1.14)[1)] obtained in the reaction of *N*-*t*-butyl-*N*-chloro-*n*-pentanesulfonamide in an aqueous solution. In the decomposition of *N*-bromosulfonamides in the aqueous solution, the low yield of conversion to the rearranged products is due to the unstability of *N*-bromosulfonamides in the aqueous solution and to the reduction to the original sulfonamides. Several sultam derivatives were obtained by the treatment of rearranged products with ethanolic NaOH (see Experimental Section).

Experimental

Apparatus. The glpc analyses were conducted by a Shimadzu GC-3A using Apieson L grease 10% or Silicone oil 550 10% on Diasolid L, 60—80 mesh, 1 m column. The Hg lamp was an Eikosha 150 W high-pressure Hg lamp.

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

General Procedure of N-*Bromination.* *N*-Alkyl-*n*-alkanesulfonamide (0.05 mol) was suspended in a buffer solution (100ml, pH=6.6), and to the solution, a 50-ml portion of aqueous NaOBr (freshly prepared from Br_2 (24 g) and Na_2CO_3 (16 g)) was added; the solution was then stirred for 4 hr at room temperature. The insoluble oil separated as a lower layer was collected and dissolved in CCl_4 and dried over Na_2SO_4, and the solvent was evaporated. Yield, 75—80%.

Photodecomposition of N-*Bromosulfonamides.* *N*-Bromosulfonamides were irradiated at 28—30°C under N_2 until the active bromine was negligible.

Isolation and Analyses of Reaction Products. Analyses of the products in the reaction of *N*-bromo-*N*-*t*-butylbutanesulfonamide, the alkali treatment, and analyses of sultams were carried out as has been described in our previous papers.[1,3)]

N-t-*Butyl-γ-bromo*-n-*propanesulfonamide.* This substance was obtained by adding hexane to an ether solution of reaction products and was recrystallized from cold ether. Mp 76°C. IR: 3285, 2960, 1315, and 1135 cm^{-1}, NMR (in $CDCl_3$): τ; 5.45 (1H), 6.45(triplet, 2H), 6.80(triplet, 2H), 7.65(multiplet, 2H), 8.62(singlet, 9H).

Found: C, 32.80; H, 6.20; N, 5.25; Br, 30.8%. Calcd for $C_7H_{16}BrNO_2S$: C, 32.57; H, 6.25; N, 5.43; Br, 30.95%.

N-t-*Butylpropanesultam.* This was obtained by the ethanolic treatment of *N*-*t*-butyl-γ-bromopropanesulfonamide with ethanolic NaOH. Yield, 96%. Mp 56°C. IR: 2960, 1310, 1210, 1130, 1000, and 730 cm^{-1}. NMR (in $CDCl_3$): τ; 6.55—6.98 (multiplet, 4H), 7.55—7.90(multiplet, 2H), 8.63(singlet, 9H).

Found: C, 47.46; H, 8.51; N, 7.72%. Calcd for $C_7H_{15}NO_2S$: C, 47.43; H, 8.53; N, 7.90%.

N-t-*Butyl-δ-bromo*-n-*pentanesulfonamide.* This was obtained by cooling the hexane solution of the reaction mixture and was recrystallized from cold ether. Mp 55°C. IR: 3280, 2960, 1310, and 1130 cm^{-1}. NMR(in $CDCl_3$):τ; 5.60(1H), 5.95(multiplet, IH), 6.95(triplet, 2H), 8.05(multiplet, 4H), 8.25(doublet, 3H), 8.62(singlet, 9H).

Found: C, 37.44; H, 7.24; N, 4.85; Br, 27.7%. Calcd for $C_9H_{20}BrNO_2S$: C, 37.77; H, 7.04; N, 4.89; Br, 27.91%.

The alkali treatment of this product gave *N*-*t*-butylpent-3-enesulfonamide.[1)] Yield, 91%.

N-t-*Butyl-γ-bromo*-n-*pentanesulfonamide.* The presence of this isomer was confirmed by the formation of *N*-*t*-butyl-3-ethylpropanesultam[3)] by the alkali treatment of the reaction mixture obtained after the removal of the δ-bromo isomer.

N-t-*Butyl-δ-bromo*-n-*hexanesulfonamide (II).* On cooling the hexane solution of the products to −50°C, a white precipitate was obtained; this was shown to be a mixture of two isomers by glpc and elementary analyses. On the cooling of an ether solution of this mixture, II was isolated and recrystallized from ether and hexane. Mp 63°C. IR: 3280, 2960, 1320, and 1140 cm^{-1}. NMR(in CCl_4): τ; 4.85(1H), 6.05(multiplet, 1H), 7.00 (multiplet, 2H), 7.80—8.30 (multiplet, 6H), 8.62 (singlet, 9H), 8.93(triplet, 3H).

Found: C, 40.16; H, 7.43; N, 4.59; Br, 26.5%. Calcd for $C_{10}H_{22}BrNO_2S$: C, 40.00; H, 7.39; N, 4.67; Br, 26.61%.

4-Ethylbutanesultam[1)] was obtained by the alkali treatment of the δ-bromohexanesulfonamide produced by the treatment of II with HCl in a similar manner to that described in a previous paper.[1)] Yield, 87%.

N-t-*Butyl-γ-bromo*-n-*hexanesulfonamide (I).* When the hexane solution of the filtrate was cooled to −70°C after the

3) M. Okahara, T. Ohashi, and S. Komori, *J. Org. Chem.*, **33**, 3066 (1968).

the removal of the δ-bromo isomer, I was isolated as a white precipitate which melted at room temperature. n_D^{20} 1.4838. IR: 3280, 2960, 1320, and 1140 cm^{-1}. NMR (in CCl_4): τ; 4.75(1H), 5.95 (multiplet, 1H), 6.90(triplet, 2H), 7.60—8.35 (multiplet, 6H), 8.63 (singlet, 9H), 9.00 (triplet, 3H).

Found: C, 40.30; H, 7.54; N,4.26; Br, 26.4%. Calcd for $C_{10}H_{22}BrNO_2S$; C, 40.00; H, 7.39; N, 4.67; Br, 26.61%.

3-Propylpropanesultam[1] was obtained from I in the same manner as has been described above. Yield, 80%.

N-*Methyl-γ-bromo*-n-*butanesulfonamide.* The presence of this compound was confirmed by a study of the NMR of the reaction mixture. NMR (in $CDCl_3$): τ; 5.85(multiplet, CHBr), 8.25(doublet, CH_3CHBr).

Furthermore, the formation of *N*-methyl-3-mehtylpropanesultam was observed by glpc and NMR of the products obtained by the alkali treatment of the reaction mixture described above.

N-*Methyl-3-methylpropanesultam.* An authentic sample of this sultam was obtained by the alkali treatment of *N-methyl-γ*-chloro-*n*-butanesulfonamide.[1] Bp 78—80°C/0.2mmHg, n_D^{32} 1.4660. IR: 2960, 1310, 1140, 1050, 930, 845, and 755cm^{-1}. NMR(in $CDCl_3$): τ; 6.65—7.05(mutiplet, 3H), 7.40(singlet, 3H), 7.50-8.10(multiplet, 2H), 8.72(doublet, 3H).

Found: C, 39.96; H, 7.12; N, 9.40%. Calcd for $C_5H_{11}NO_2S$: C, 40.26; H, 7.43; N, 9.39%.