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Reaction of N-Haloamide. XXV.[1] Addition Reaction of N,N-Dibromobenzenesulfonamide with Asymmetric Olefins and α,β-Unsaturated Carboxylic Acid Esters[2]

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In order to confirm the orientation of the addition of N,N-dibromobenzenesulfonamide (DBBS) to olefins, the reactions of DBBS with asymmetric alkenes and α,β-unsaturated carboxylic acid esters were examined.

The additions of DBBS to alkenes proceeded by Markownikoff's fashion, and those to the unsaturated esters gave the products which have bromines at α-carbons and sulfonamido groups at β-positions. The reactions of DBBS with 1-methylcyclohexene, 2,3-dimethyl-1-butene, and 1,1-dimethyl-1-butene gave I, III, and IV, respectively. The reactions of DBBS with methyl methacrylate, methyl acrylate, and methyl crotonate gave V and VI, VIII and IX, and XI and XII, respectively.

In the previous papers,[4] we reported on the addition reactions of N,N-dibromobenzenesulfonamide (DBBS) with cyclohexene and cyclopentene.

Foglia and his coworkers[5] have published a study on the addition of N,N-dichlorourethan (DCU) to asymmetric alkenes. In their report, the products were found to be anti-Markownikoff adducts, hence they assumed that the reactions include free radical mechanism. On the other hand, they have described that the addition of DCU to compounds which have double bonds linked to electron-withdrawing groups such as CN or COOR gave β-chlorocarbamates in which the chlorine atoms were attached to the carbons adjacent to the electron-withdrawing groups, therefore, they claimed, in this case, that the reactions proceeded in ionic rather than radical mechanism.[5] In spite of these conclusion, the addition of DCU to ethyl cinnamate gave an adduct having halogen in the benzyl position.[5] Kharash, *et al.*[6] have reported that N,N-dibromoarylsulfonamides added to styrene by Markownikoff's fashion to give 1-bromo-2-phenyl-2-arylsulfonamidoethanes.

Otsuki, *et al.*[7] have presented that DBBS reacted with ethyl cinnamate affording an addition product which have a halogen atom at the carbon adjacent to the carbonyl group.

In the present work, we studied on the orientation of addition of DBBS to several kinds of asymmetric alkenes and α,β-unsaturated carboxylic esters. The addition of DBBS to asymmetric alkenes proceeded by Markownikoff's fashion and that to α,β-unsaturated carboxylic esters gave bromosulfonamides in which bromine atoms were attached to the carbons adjacent to the carbonyl groups. Table I shows the structures, melting points, and yields of the β-bromosulfonamides. It is interesting that the mode of addition of DBBS to asymmetric alkenes seems to be different from that of DCU. In the reaction of DBBS with asymmetric

1) Part XXIV: H. Terauchi and S. Takemura, *Chem. Pharm. Bull.* (Tokyo), **23**, 2410 (1975).
2) A part of this work was presented at the 95th Annual Meeting of the Pharmaceutical Society of Japan, Nishinomiya, April, 1975.
3) Location: *Kowakae, Higashi-osaka.*
4) Y. Ueno, S. Takemura, Y. Ando, and H. Terauchi, *Chem. Pharm. Bull.* (Tokyo), **15**, 1193, 1198, 1328 (1967).
5) T.A. Foglia and D. Swern, *J. Org. Chem.*, **33**, 766 (1968).
6) M.S. Kharash and H.M. Priestley, *J. Am. Chem. Soc.*, **61**, 3425 (1939).
7) K. Otsuki, K. Okamoto, S. Takemura, and Y. Ueno, presented at the 32nd Meeting of the Tohoku-branch of the Pharmaceutical Society of Japan, 1969, Sendai.

alkenes, one molar DBBS in dichloromethane was added to a solution of four molar alkenes in the same solvent at −20°. After the addition, the reaction mixture was still positive for potassium iodide-starch test by the presence of N-bromo-intermediate as observed in the reaction of DBBS with cyclohexene.[4] After the treatment of the mixture with sodium bisulfite solution, the addition products and benzenesulfonamide were isolated in the yields of 16—35% and 30—45%, respectively.

The reaction of 1-methyl-1-cyclohexene with DBBS gave an adduct (I), $C_{13}H_{18}O_2NSBr$. It exhibited an NH band in the infrared (IR) spectrum. The nuclear magnetic resonance (NMR) spectral assignments were shown in Table II. Compound I was converted to II by the

Table I. Addition Products of DBBS to Asymmetric Alkenes and α,β-Unsaturated Carboxylic Acid Esters

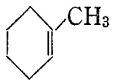
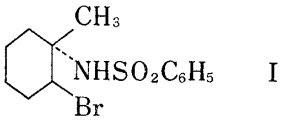
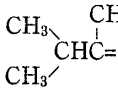
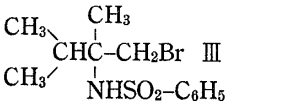
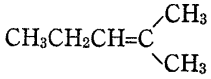
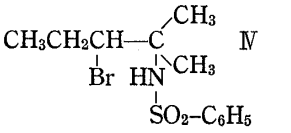
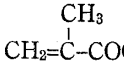
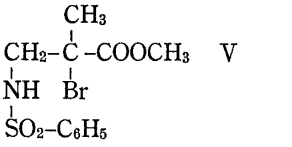
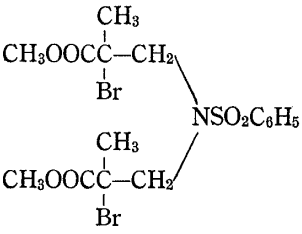
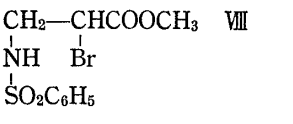
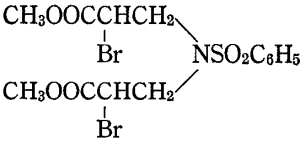
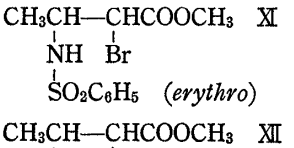
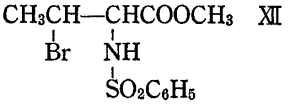
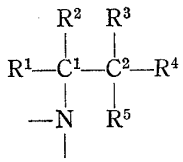
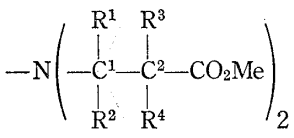
Unsaturated compound	Addition product	mp (°C)	Yield (%)
	 I	151—153	35
	 III	147—149	16
	 IV	80—82	22
	 V	82—83	59
	 VI	89—90	12
CH_2=CHCOOCH$_3$	 VII	66—68	69
	 IX	74—76	7.9
CH_3CH=CHCOOCH$_3$	 XI (*erythro*)	123—125	30
	 XII	86—88	3

TABLE II. NMR Specttal Assignments of Products



Compound	R^1	R^2	R^3	R^4	R^5	Chemical shift (ppm, TMS=0) of protons attached to		
						C^1	C^2	N
I	CH_3	$-(CH_2)_4-$		H	Br	—	4.32q[a]	5.10s
II	CH_3	$-(CH_2)_4-$		H	(N)	—	3.09q[a]	—
III (Fig. 1)	$(CH_3)_2CH$	CH_3	H	H	Br	—	3.65d[a] (J=10 Hz) 3.43 d[a] (J=10 Hz)	4.95s
IV	CH_3	CH_3	CH_3CH_2	H	Br	—	4.05q[a,b] (J=2.3 Hz, J_2=10 Hz)	5.90s
V	H	H	CH_3	CO_2Me	Br	3.48d[c] (J_1=8 Hz) D_2O: s[d] 3.51d[c] (J=7 Hz) D_2O: s[d]	—	5.32 t, br
VIII	H	H	H	CO_2Me	Br	3.50 m D_2O: 2d[d] (J=7 Hz)	4.38t[a] (J=7 Hz)	5.77t (J=6 Hz)
XI (Fig. 2)	CH_3	H	H	CO_2Me	Br	3.92 m[e]	4.40d[a] (J=4.5 Hz)	5.43d
XII (Fig. 4)	CO_2Me	H	H	CH_3	Br	4.15q[e] (J_1=2.5 Hz, J_2=10 Hz) D_2O: d (J=2.5 Hz)	4.52 m[a,e]	5.47d, br
XIII (Fig. 3)	CH_3	H	H	CO_2Me	(N)	3.10 m[e]	3.35d[a] (J=4.4 Hz)	—



Compound	R^1	R^2	R^3	R^4	Chemical shifts (ppm, TMS=0) of protons attached to		
					C^1	C^2	N
VI	H	H	CH_3	Br	3.85br[f] (4H)	$2CH_3(R^3)$: 2.0s	—
VII	H	H	CH_3	H	3.30d,br (4H)	2.90 m (R^4, $2H_3$) $2CH_3(R^3)$: 1.15d (J=7 Hz)	— —
IX	H	H	H	Br	3.75 m[f] (4H)	4.64t (2H)	— —
X	H	H	H	H	3.49t (4H)	2.62t (4H)	— —

a) showed no change by D_2O-treatment, *b*) X part of ABX type coupling, *c*) changed to singlet by D_2O-treatment, *d*) an observed part of AB doublet of ABX type splitting, *e*) The changes by decoupling were described in the text and shown in the figures. *f*) overlapped with OCH_3-proton signals

treatment with 5% sodium hydroxide giving colorless crystals, $C_{13}H_{17}O_2NS$. The NH band of I in the IR disappeared by this treatment. The assignment of the chemical shift was shown in Table II. On the basis of the analogy with the product of the addition of DBBS to cyclo-

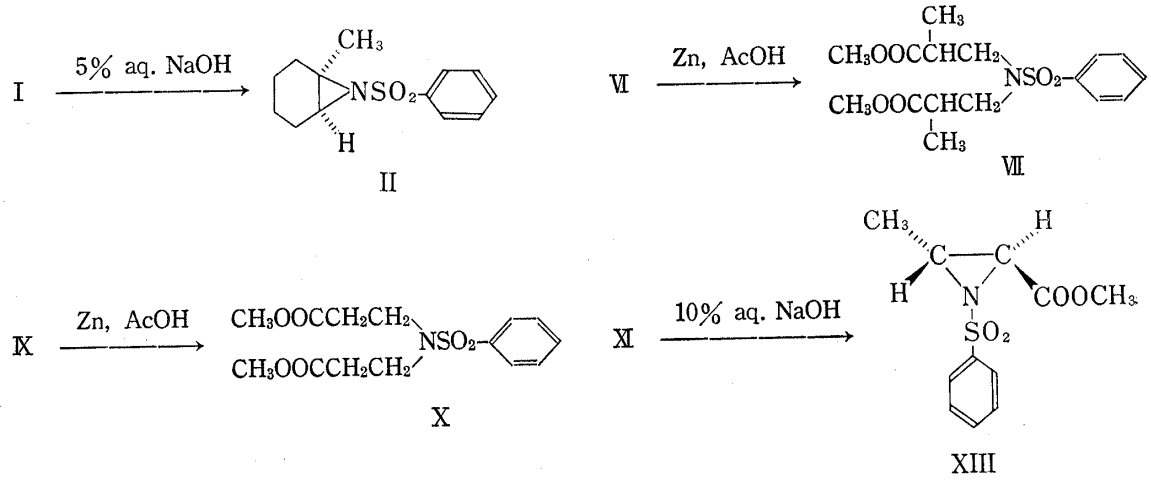


Chart 1

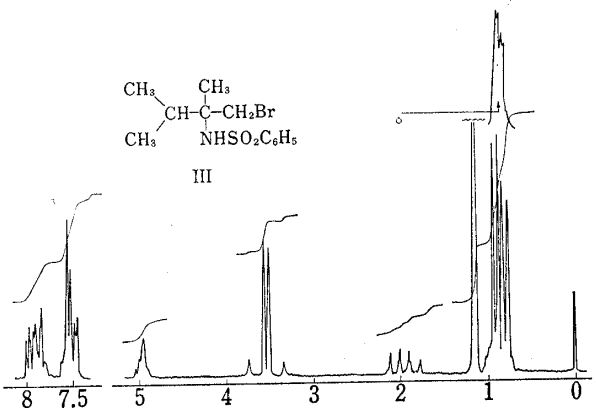


Fig. 1. NMR Spectrum of 1-Bromo-2,3-dimethyl-2-benzenesulfonamidobutane (III) at 60 MHz in $CDCl_3$

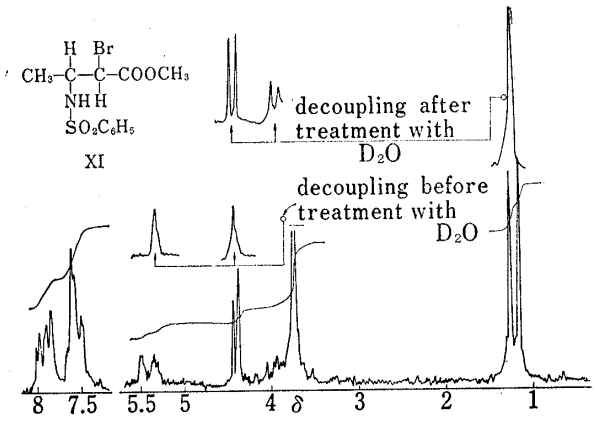


Fig. 2. NMR Spectrum of Methyl *erythro*-α-Bromo-β-benzenesulfonamidobutylate (XI) at 60 Mc in $CDCl_3$

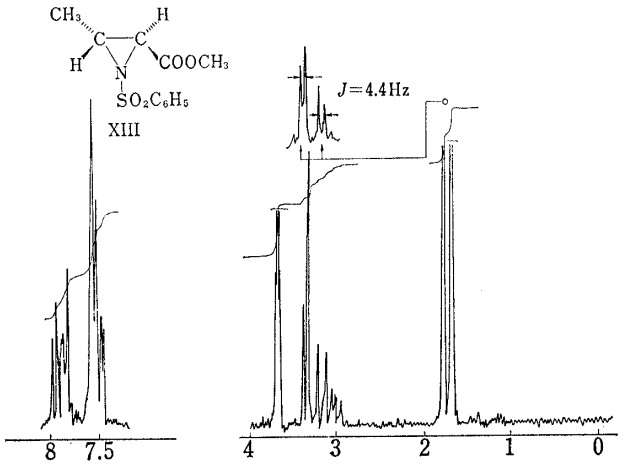


Fig. 3. NMR Spectrum of *trans*-2-Carbomethoxy-N-benzenesulfonylaziridine (XIII) at 60 Mc in $CDCl_3$

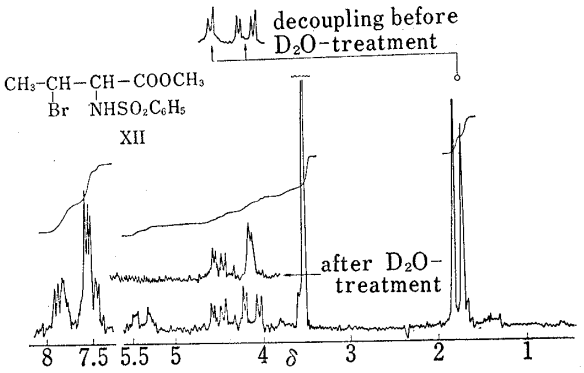


Fig. 4. NMR Spectrum of Methyl α-Benzenesulfonamido-β-bromobutylate (XII) at 60 Mc in $CDCl_3$

hexene[4] and the spectral data, compound II was presumed to be 1-methyl-N-benzenesulfonylcyclohexeneimine (Chart 1). The formation of II by the treatment of I with alkali indicates the *trans*-configuration of the benzenesulfonamido group and bromine in I. Consequently, the structure of 2-bromo-1-methyl-1-benzenesulfonamidocyclohexane was given for I.

The reaction of 2,3-dimethyl-1-butene with DBBS gave an adduct (III), $C_{12}H_{18}O_2NSBr$. The IR spectrum of III showed the presence of NH group. In its NMR spectrum (Fig. 1 and Table II), the AB type doublets at 3.65 and 3.43 ppm were not affected by deuterium oxide treatment. This indicates the absence of proton on the carbon bearing NH group. As shown in Fig. 1, decoupling by irradiation at 1.95 ppm, the signal of the methine proton, caused changes of two methyl proton-doublets, 0.87 and 0.82 ppm, to singlets, while the doublets at 3.65 and 3.43 ppm were not affected. On the basis of these spectral data, the structure, 1-bromo-2,3-dimethyl-2-benzenesulfonamidobutane, was given for III.

The reaction of 1,1-dimethyl-1-butene with DBBS gave an addition product (IV), $C_{12}H_{18}O_2NSBr$. It showed an NH stretching absorption in the IR spectrum. The NMR spectral assignments were given in Table II. A signal centered at 1.85 ppm integrated as two protons was presumed to be H_A and H_B-parts of the ABX coupling and this signal seemed to be complicated because of the additional coupling with adjacent methyl protons. On the above spectral data, compound IV was assigned to the structure, 1,1-dimethyl-1-benzenesulfonamido-2-bromobutane.

The reaction of α,β-unsaturated carboxylic ester with DBBS required to reflux in dichloromethane for 2 hours to complete. After the reaction mixture had been treated with sodium bisulfite solution to reduce remaining active bromine, the addition products were isolated in the yields of 30—69%.

The reaction of methyl methacrylate with DBBS gave addition products, (V) $C_{11}H_{14}O_4NSBr$, and (VI) $C_{16}H_{21}O_6NSBr_2$. The IR spectrum of V indicated the presence of an NH group, and the NMR spectrum showed signals given in Table II. The singlets observed by deuterium oxide-treatment were assumed to be a part of a set of AB doublets. On the basis of the spectral data, the structure of V was presumed to be methyl α-bromo-α-methyl-β-benzenesulfonamidopropionate.

Compound VI showed no NH absorption band in the IR region. Compound VI was refluxed with zinc dust in acetic acid to obtain a dehalogenated oily product (VII) $C_{16}H_{23}O_6NS$, bp_5 190°. In the NMR spectrum of VI, a broad signal corresponding to ten protons was assigned to be a overlapping signal of four C^1-protons and two ester methyl protons (Table II). Compound VII exhibited a somewhat broad doublet corresponding to four protons at 3.30 ppm which was assigned to four protons on C^1 (Table II), and a multiplet corresponding to two protons assigned to newly formed C^2-protons appeared at 2.90 ppm. These complexity of the signal is probably due to the presence of diastereoisomers in VII, accordingly, compound VI may also be a mixture of meso and racemi isomers. Thus, the plane structures shown in Table I and Chart I were given for VI and VII, respectively.

In the reaction of methyl acrylate with DBBS, addition products, (VIII) $C_{10}H_{12}O_4NSBr$ and (IX) $C_{14}H_{17}O_6NSBr_2$, were obtained. Compound VIII showed an NH absorption band in the IR spectrum. The NMR spectrum of it exhibited signals shown in Table II. Among them, the multiplet at 3.50 ppm was observed to be changed by D_2O-treatment to two doublets which were assumed to be a part of a set of AB splitting in ABX coupling. Thus the structure of VIII was presumed as shown in Table I. Compound IX lacked NH absorption band in its IR spectrum. The assignments of the NMR signals of IX were shown in Table II. The multiplet at 3.75 ppm which was assigned to C^1-protons was partially overlapped with the signal of the ester methyls, and the triplet at 4.64 ppm which was assigned to C^2-protons was accompanied by a small triplet in detail. These facts suggest that IX is a mixture of considerable amount of diastereoisomers. Reduction of IX with zinc dust in acetic acid gave a dehalogenated product, (X) $C_{14}H_{19}O_6NS$, bp_5 190—200°. The NMR spectrum of X exhibited signals as shown

in Table II. From these fact, the structures of IX and X were assigned to them as shown in Table I and Chart I, respectively.

The reaction of methyl crotonate with DBBS gave two kinds of adducts, (XI) $C_{11}H_{14}O_4NSBr$ and (XII) $C_{11}H_{14}O_4NSBr$. The product XI showed an NH absorption band in its IR spectrum. Its NMR spectrum was shown in Fig. 2 and the data was given in Table II. Decoupling by irradiation at 3.92 ppm before treatment with D_2O caused a change of the doublets at 5.43 and 4.40 ppm to singlets. After addition of deuterium oxide, decoupling irradiating 1.20 ppm gave no change of the doublet at 4.40 ppm while the multiplet at 3.92 ppm changed into a doublet (J=4.5 Hz) (Fig. 2). Compound XI was treated with 10% aqueous sodium hydroxide at room temperature to give an oil (XIII), bp_3 170—80°, $C_{11}H_{13}O_4NS$, which showed no NH absorption band in the IR spectrum. The NMR spectral assignments (Table II) were given by the use of decoupling technique, *i.e.*, irradiation at 1.73 ppm caused a change of the signal at 3.10 ppm to a doublet (J=4.4 Hz) (Fig. 3).

Greatbanks, *et al.*[8] described that the coupling constants of vicinal protons of imine ring were observed as 7.0 Hz for *cis*-aziridine while 4.2 Hz for *trans* one being based upon the NMR spectra of *cis*- and *trans*-2-*p*-methoxyphenyl-3-methyl-N-(N′,N′-dimethylsulfonyl)-aziridines. The coupling constant of vicinal ring protons of compound XIII, J=4.4 Hz, is close to the value of *trans*-aziridine. Therefore, compound XIII was given the structure of *trans*-2-carbomethoxy-3-methyl-N-benzenesulfonylaziridine. The fact that the aziridine, XIII, was obtained from XI indicates that the bromine atom and benzenesulfonamido group in XI are linked in *erythro* configuration. On the basis of the above results, the structure, methyl *erythro*-α-bromo-β-benzenesulfonamidobutylate, was given for compound XI.

The another product, XII, showed an NH band in the IR spectrum. The NMR spectrum of this product (Fig. 4) exhibited a set of signals shown in Table II. Irradiation at 1.75 ppm did not change the quartet at 4.15 ppm, and caused a change of the multiplet at 4.52 ppm to a doublet (J=2.5 Hz) (Fig. 4). Thus the structure of XII was presumed to be methyl α-benzenesulfonamido-β-bromobutylate. The configuration of the bromine and benzenesulfonamido group in XII could not confirmed because of the poor yield. Besides of XI and XII, benzenesulfonamide was isolated from the reaction mixture in 30% yield.

Experimental

Reaction of 1-Methylcyclohexene with DBBS and Isolation of I——A solution of DBBS (14.2 g, 0.043 mole) in CH_2Cl_2 (150 ml) was added to a solution of 1-methylcyclohexene (16.6 g, 0.173 mole) in CH_2Cl_2 (100 ml) with stirring in a period of 1 hr at −20°. The stirring was continued for additional 1.5 hr at 0—10°. The pale yellow reaction mixture was then stirred with an aqueous solution of $NaHSO_3$ until KI-starch test showed negative. The organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated. The residue was chromatographed on a silica gel column eluting with a mixture of $CHCl_3$ and *n*-hexane (1: 4) to give colorless crystals of I (5 g), mp 151—153° (from CCl_4). IR_{max}^{Nujol} cm^{-1}: 3250 (ν_{NH}), 1325, 1159 (ν_{SO_2N}). NMR ($CDCl_3$) δ: 7.70 (5H, C_6H_5), 5.10 (1H, s, NH), 4.32 (1H, q, J_1=5 Hz, J_2=10 Hz, CHBr), 1.64 (8H, protons of cyclohexane ring), 1.3 (3H, s, C–CH_3). *Anal.* Calcd. for $C_{13}H_{18}O_2NSBr$: C, 46.99; H, 5.47; N, 4.22. Found: C, 46.94; H, 5.23; N, 4.21. After the elution of I, successive elution of the column with MeOH gave benzenesulfonamide (3 g).

Conversion of I to Aziridine II——A solution of I (0.5 g) in $CHCl_3$ (20 ml) was stirred with 5% aq. NaOH (20 ml) at room temperature for 1 hr. The lower phase separated was washed with water, dried over Na_2SO_4, and the solvent was distilled off under reduced pressure to leave colorless crystals of II (0.30 g, 81%), mp 30—32° (from CCl_4). IR_{max}^{Nujol} cm^{-1}: 1300, 1140 (ν_{SO_2N}). NMR ($CDCl_3$) δ: 7.70 (5H, C_6H_5), 3.06 (1H, q, J_1=1.5 Hz, J_2=5 Hz, CHN), 1.70 (3H, s, C–CH_3), 1.65 and 1.35 (4H, and 4H, m, protons of cyclohexane ring). *Anal.* Calcd. for $C_{13}H_{17}O_2NS$: C, 62.12; H, 6.82; N, 5.57. Found: C, 62.64; H, 7.10; N, 5.70.

Reaction of 2,3-Dimethyl-1-butene with DBBS and Isolation of III——DBBS (9.4 g, 0.03 mole) in CH_2Cl_2 (60 ml) was added to a solution of 2,3-dimethyl-1-butene (10 g, 0.12 mole) in CH_2Cl_2 (60 ml) with stirring in a period of 2 hr at −20°. Additional stirring was continued for 1 hr. The mixture was stirred with aq. $NaHSO_3$ until KI-starch test turned negative, washed with water, dried over Na_2SO_4, and concentrated

8) D. Grreatbanks, T.P. Seden, and R.W. Turner, *Tetrahedron Letters*, **1968**, 4863.

in vacuo to obtain benzenesulfonamide (2.1 g, 45%) and an oil which was chromatographed on a silica gel column eluting with a mixture of $CHCl_3$: *n*-hexane (1: 4) to give colorless crystals of III (1.5 g), mp 147—149° (from 95% EtOH). NMR of III is shown in Fig. 1. IR_{max}^{Nujol} cm^{-1}: 3250 (ν_{NH}), 1310, 1150 (ν_{SO_2N}). *Anal.* Calcd. for $C_{12}H_{18}O_2NSBr$: C, 45.00; H, 5.66; N, 4.37. Found: C, 45.10; H, 5.66; N, 4.41.

Reaction of 1,1-Dimethyl-1-butene with DBBS and Isolation of IV——A solution of DBBS (9.45 g, 0.03 mole) in CH_2Cl_2 (60 ml) was added to the mixture of 1,1-dimethyl-1-butene (10 g, 0.12 mole) and CH_2Cl_2 (60 ml) in a period of 2 hr at −20° and the stirring was continued for additional 1 hr. The clear yellow solution obtained was treated with aq. $NaHSO_3$ to reduce active halogen, washed with H_2O, dried over Na_2SO_4, and concentrated to obtain benzenesulfonamide (1.5 g, 30%) and crude IV which was purified through a silica gel column eluting with $CHCl_3$: *n*-hexane (1: 4). IV obtained from the eluate was recrystallized from *n*-hexane, mp 80—82° (2.1 g). IR_{max}^{Nujol} cm^{-1}: 3200 (ν_{NH}), 1310, 1150 (ν_{SO_2N}). NMR (CCl_4) δ: 7.55 (5H, C_6H_5), 5.90 (1H, s, NH), 4.05 (1H, q, $J_1=2.3$ Hz, $J_2=10$ Hz, CHBr), 1.85 (2H, m, CH_2), 1.05—1.30 (9H, $3\times$C–CH_3). *Anal.* Calcd. for $C_{12}H_{18}O_2NSBr$: C, 44.99; H, 5.67; N, 4.37. Found: C, 44.96; H, 5.84; N, 4.28.

Reaction of Methyl Methacrylate with DBBS and Isolation of V and VI——A solution of DBBS (5 g, 0.015 mole) in CH_2Cl_2 (20 ml) was dropwise added to the solution of methyl methacrylate (7.95 g, 0.08 mole) in CH_2Cl_2 (20 ml) with stirring at 0° in a period of 1 hr. The mixture was then refluxed for 2 hr, and treated with aq. $NaHSO_3$ to reduce active halogen. The CH_2Cl_2-layer separated was washed with H_2O, dried (Na_2SO_4), and the solvent was removed by distillation. The residue was applied to chromatography on a silica gel column eluted with $CHCl_3$: *n*-hexane (1: 4). The first fraction gave colorless crystals of VI (1.04 g), mp 89—90° (from CCl_4). IR_{max}^{Nujol} cm^{-1}: 1730 ($\nu_{C=O}$), 1330, 1130 (ν_{SO_2N}). NMR ($CDCl_3$) δ: 7.65 (5H, C_6H_5), 3.85 (10H, s, $2\times COOCH_3$, and a broad signal of $2\times CH_2$), 2.0 (6H, s, $2\times$C–CH_3). *Anal.* Calcd. for $C_{16}H_{21}O_6NSBr_2$: C, 37.29; H, 4.07; N, 2.71. Found: C, 37.01; H, 4.02; N, 2.37.

Further elution of the column with said solvent gave colorless crystals of V (3.31 g), mp 82—83° (from CCl_4). IR_{max}^{Nujol} cm^{-1}: 3200 (ν_{NH}), 1720 ($\nu_{C=O}$), 1330, 1130 (ν_{SO_2N}). NMR ($CDCl_3$) δ: 7.6 (5H, C_6H_5), 5.35 (1H, broad t, NH), 3.75 (3H, s, $COOCH_3$), 3.51 (1H, d, $J=7$ Hz, CHNH, s, CHND by addition of D_2O), 3.48 (1H, d, $J=8$ Hz, CHNH, s, by treatment with D_2O), 1.92 (3H, s, C–CH_3). *Anal.* Calcd. for $C_{14}H_{14}O_4NSBr$: C, 39.29; H, 4.16; N, 4.16. Found: C, 39.45; H, 4.34; N, 4.20. Besides isolation of the main products, V and VI, a small amount of oily product was isolated from the reaction mixture, however it was difficult to perform further studies.

Reductive Debromination of VI to VII——The mixture of VI (0.5 g, 0.001 mole), Zn powder (0.5 g), and AcOH (1 ml) was heated to boil for 1 hr. After cooling, the mixture was poured into H_2O (50 ml) and extracted with $CHCl_3$. The extract was washed with 10% aq. Na_2CO_3 followed by H_2O, dried (Na_2SO_4), and $CHCl_3$ was distilled to leave crude VII. Crude VII was distlled, bp_5 190°, to obtain pure sample (0.24 g, 85%). IR_{max}^{Nujol} cm^{-1}: 1735 ($\nu_{C=O}$), 1330, 1150 (ν_{SO_2N}), NMR ($CDCl_3$) δ: 7.65 (5H, C_6H_5), 3.70 (6H, s, $COOCH_3$), 3.30 (4H, d, $J=7.5$ Hz, CH_2NCH_2), 2.90 (2H, m, $2\times$CHCO), 1.15 (6H, d, $J=7.0$ Hz, $2\times$C–CH_3). *Anal.* Calcd. for $C_{16}H_{23}O_6NS$: C, 53.78; H, 6.44; N, 3.92. Found: C, 53.56; H, 6.75; N, 4.20.

Reaction of Methyl Acrylate with DBBS and Isolation of VIII and IX——To the solution of methyl acrylate (13.6 g, 0.16 mole) in CH_2Cl_2 (40 ml), DBBS (10 g, 0.03 mole) in CH_2Cl_2 (40 ml) was added at 0°. The mixture was refluxed for 2 hr, and treated with aq. $NaHSO_3$ to reduce active bromine. The solution was washed with H_2O, dried over Na_2SO_4, and the solvent was removed to obtain crude addition product which was passed through a silica gel column using a mixed solvent of $CHCl_3$: *n*-hexane (1: 4) to give a product IX (1.2 g), mp 74—76° (from EtOH). IR_{max}^{Nujol} cm^{-1}: 1740 ($\nu_{C=O}$), 1335, 1130 (ν_{SO_2N}). NMR ($CDCl_3$) δ: 7.70 (5H, C_6H_5), 4.64 (2H, t, $J=7$ Hz, $2\times$CHBr), 3.80 (6H, s, $2\times COOCH_3$), 3.85—3.65 (4H, m, CH_2NCH_2). *Anal.* Calcd. for $C_{14}H_{17}O_6NSBr_2$: C, 34.50; H, 3.52; N, 2.80. Found: C, 34.26; H, 3.42; N, 2.96.

Successive elution of the said column gave colorless crystals of VIII (6.6 g), mp 66—68° (from CCl_4). IR_{max}^{Nujol} cm^{-1}: 3300 (ν_{NH}), 1720 ($\nu_{C=O}$), 1320, 1130 (ν_{SO_2N}). NMR ($CDCl_3$) δ: 7.70 (5H, C_6H_5), 5.77 (1H, t, $J=$ 6 Hz, NH), 4.38 (1H, t, $J=7$ Hz, CHBr), 3.50 (2H, sextet, CH_2NH, 2d, $J=7$ Hz, CH_2ND by addition of D_2O), 3.75 (3H, s, $COOCH_3$). *Anal.* Calcd. for $C_{10}H_{12}O_4NSBr$: C, 37.28; H, 3.75; N, 4.35. Found: C, 37.58; H, 4.01; N, 4.20. A by-product, an oil found in the reaction mixture, was difficult to perform further purification because of its poor yield.

Reductive Debromination of IX to X——Compound IX (1 g) was refluxed with Zn (1 g) and AcOH (2 ml) for 1 hr. The mixture was poured into H_2O (100 ml), and extracted with $CHCl_3$. The $CHCl_3$-layer separated was washed with 10% aq. Na_2CO_3 followed by H_2O, dried (Na_2SO_4), and the solvent was removed to leave X which was distilled, bp_5 190—200° (0.24 g, 40%). IR_{max}^{Nujol} cm^{-1}: 1730 ($\nu_{C=O}$), 1330, 1150 (ν_{SO_2N}). NMR ($CDCl_3$) δ: 7.70 (5H, C_6H_5), 3.68 (6H, s, $2\times COOCH_3$), 3.49 (4H, t, $J=7.5$ Hz, $2\times CH_2$), 2.62 (4H, t, $J=7.5$ Hz, $2\times CH_2$). *Anal.* Calcd. for $C_{14}H_{19}O_6NS$: C, 51.04; H, 5.82; N, 4.25. Found: C, 50.87, H, 6.14; N, 4.46.

Reaction of Methyl Crotonate with DBBS and Isolation of XI and XII——DBBS (10 g, 0.03 mole) in CH_2Cl_2 (40 ml) was dropwise added to a solution of methyl crotonate (15.9 g, 0.15 mole) in CH_2Cl_2 (40 ml) at 0°. The reaction mixture was then refluxed for 2 hr, treated with aq. $NaHSO_3$ to reduce remaining active halogen, washed with H_2O, dried over Na_2SO_4, and concentrated. The residue was chromatographed on a silica gel column using a solvent of $CHCl_3$: *n*-hexane (1: 4). From the first eluate, colorless crystals of XII (0.3 g), mp 86—88° (from *n*-hexane) were obtained. IR_{max}^{Nujol} cm^{-1}: 3250 (ν_{NH}), 1720 ($\nu_{C=O}$), 1330, 1140 (ν_{SO_2N}). NMR

($CDCl_3$) was shown in Fig. 4. *Anal.* Calcd. for $C_{11}H_{14}O_4NSBr$: C, 39.28; H, 4.20; N, 4.17. Found: C, 39.27; H, 4.18; N, 4.08. From the next eluate of the column, crystals of XI were obtained (3 g), mp 123—125° (from EtOH). IR_{max}^{Nujol} cm^{-1}: 3250 (ν_{NH}), 1730 ($\nu_{C=O}$), 1330, 1150 (ν_{SO_2N}). NMR of XI was shown in Fig. 2. *Anal.* Calcd. for $C_{11}H_{14}O_4NSBr$: C, 39.28; H, 4.20; N, 4.17. Found: C, 39.27; H, 4.08; N, 4.12.

The final elution with MeOH gave benzenesulfonamide (1.5 g, 30%).

Conversion of XI to XIII——Compound XI (1 g) was dissolved in $CHCl_3$ (20 ml), and the solution was stirred with 10% NaOH (20 ml) at room temperature for 1 hr. The $CHCl_3$-layer separated was washed with H_2O, dried over Na_2SO_4, and the solvent was removed. The residue was distilled to collect the fraction of bp_3 170—180° (0.25 g, 40%). IR_{max}^{Nujol} cm^{-1}: 1735 ($\nu_{C=O}$), 1330, 1155 (ν_{SO_2N}). NMR of XIII was shown in Fig. 3. *Anal.* Calcd. for $C_{11}H_{13}O_4NS$: C, 51.74; H, 5.14; N, 5.49. Found: C, 51.8; H, 5.18; N, 5.24.

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