[Chem. Pharm. Bull. 24(11)2803—2809(1976)]

UDC 547.541.04 : 547.538.1.04

Reaction of Propenylbenzene Derivatives and Their Analogs. I.[1] Reaction of N,N-Dibromobenzenesulfonamide with Propenylbenzene Derivatives[2]

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(Received March 10, 1976)

N,N-Dibromobenzenesulfonamide (II) was reacted with propenylbenzene (Ib), *p*-methoxypropenylbenzene (Ic), *m*-methoxypropenylbenzene (Id), 3,4-dimethoxypropenylbenzene (Ie), and 4-benzyloxy-3-methoxypropenylbenzene (If), in various molar ratios in dichloromethane. 1-Benzenesulfonamido-2-bromo-1-phenylpropane (IIIb), 1-benzenesulfonamido-2-bromo-1-(4′-methoxyphenyl)propane (IIIc), 3′-bromo-substituted analog of IIIc (IVc), 1-benzenesulfonamido-2-bromo-1-(3′-methoxyphenyl)propane (IIId), 6′-bromo-substituted analog of IIId (IVd), 1-benzenesulfonamido-2-bromo-1-(3′,4′-dimethoxyphenyl)propane (IIIe), 6′-bromo-substituted analog of IIIe (IVe), N-benzenesulfonyl-3,4-dimethoxyaniline (V′e), 6-bromo-substituted analog of V′e (Ve), 1-benzenesulfonamido-2-bromo-1-(4′-benzyloxy-6′-bromo-3′-methoxyphenyl)propane (IVf), and N-benzenesulfonyl-6-bromo-4-benzyloxy-3-methoxyaniline (Vf) were produced as main products, respectively.

Formation of the side-chain eliminated compounds (such as V′e, Ve, and Vf) has been found when reacted in a ratio of I: II of less than 1: 1, starting from 3,4-dialkoxypropenylbenzene, and the sulfonamido group substituted in the position from which the side chain was eliminated.

In our previous paper[4] we reported that the reaction of N,N-dibromobenzenesulfonamide (DBBS) with *trans*-isosafrole (Ia) afforded N-benzenesulfonyl-6-bromo-3,4-methylenedioxyaniline (Va), a compound formed by the elimination of the side chain (C_3 fragment) and substituted with benzenesulfonamido group, in addition to the adduct (IIIa) and its 6′-bromo-substituted analog (IVa) (Chart 1).

It is interesting that such an elimination compound (Va) was obtained in this addition reaction. As a step to study the conditions and mechanism of this elimination, several kinds of propenylbenzene derivatives (Ib—f) were reacted with DBBS (II). We describe here some of the information obtained from these reactions.

The reactions were carried out in various molar ratios of I with II, in the same manner as with isosafrole[4] (Ia). The yields of the reaction products are shown in Table I, and their physical constants and elemental analytical data in Table II.

The structures of IIIb—e and IVc—f were assigned as shown in Chart 1, and their configuration may be *erythro*-form, on the basis of their infrared (IR) and nuclear magnetic resonance (NMR) spectral data and elemental analytical data, and by comparison with those of IIIa and IVa, obtained from the reaction of Ia with II.[4] Benzenesulfonamide (VI) was obtained from the reaction mixtures in a molar ratio of I: II of less than 1: 1, in each case.

General procedure starting from *trans*-propenylbenzene (Ib) gave 1-benzenesulfonamido-2-bromo-1-phenylpropane (IIIb), the main product, as colorless crystals, mp 120—121°, and a

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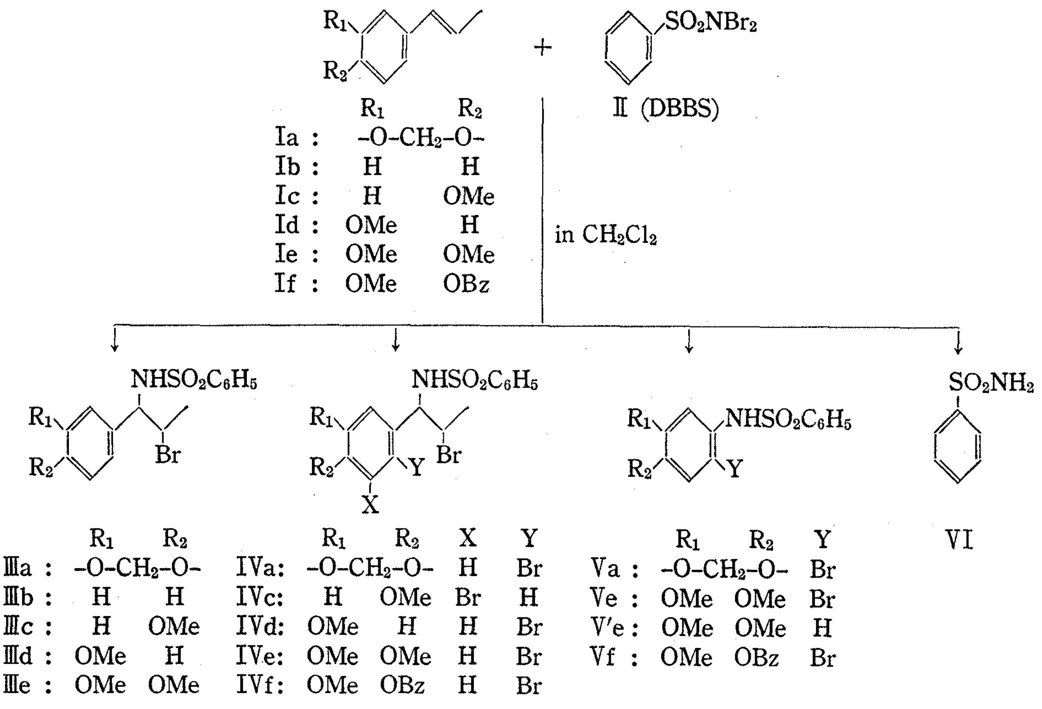
[1] This paper forms Part XXVI of "Reaction of N-Haloamide." Part XXV: H. Terauchi, A. Yamasaki, and S. Takemura, *Chem. Pharm. Bull.* (Tokyo), 23, 3162 (1975).

[2] A part of this work was presented at the 33rd Annual Meeting of the Chemical Society of Japen, Fukuoka, October, 1975.

[3] Location: *Kowakae 3-4-1, Higashiosaka, 577, Japan.*

[4] K. Otsuki and T. Irino, *Chem. Pharm. Bull.* (Tokyo), 23, 895 (1975).



	R_1	R_2
Ia :	-O-CH_2-O-	
Ib :	H	H
Ic :	H	OMe
Id :	OMe	H
Ie :	OMe	OMe
If :	OMe	OBz

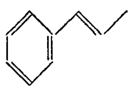
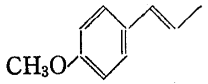
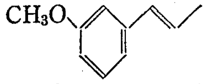
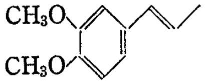
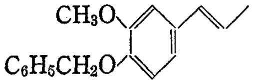
	R_1	R_2
IIIa :	-O-CH_2-O-	
IIIb :	H	H
IIIc :	H	OMe
IIId :	OMe	H
IIIe :	OMe	OMe

	R_1	R_2	X	Y
IVa:	-O-CH_2-O-		H	Br
IVc:	H	OMe	Br	H
IVd:	OMe	H	H	Br
IVe:	OMe	OMe	H	Br
IVf:	OMe	OBz	H	Br

	R_1	R_2	Y
Va :	-O-CH_2-O-		Br
Ve :	OMe	OMe	Br
V'e :	OMe	OMe	H
Vf :	OMe	OBz	Br

Chart 1

Table I. Yields (%) of the Products obtained from Reactions of I with II in Various Molar Ratios

	Starting material	Molar ratio of I:II	IIIb-e	IVc-f	Ve, f	VI
Ib		1:1	84.6	0	0	trace
		1:1.5	75.3	0	0	26.0
Ic		1:0.5	80.6	0	0	0
		1:1	80.5	0	0	trace
		1:2	0	79.3	0	58.6
Id		1:0.5	81.6	0	0	0
		1:1	27.6	45.8	0	trace
		1:1.5	0	75.4	0	28.5
Ie		1:0.75	89.9	0	0	0
		1:1	0	63.1	32.6[a]	trace
		1:1.5	0	73.2	23.7	37.7
If		1:1	0	85.7	8.3	trace
		1:1.5	0	44.6	30.6	35.0

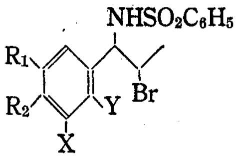
a) Ve: 18.6% V'e: 14.0%

small amount of 1,2-dibromo-1-phenylpropane (VII), the structures being assigned on the basis of its NMR and mass spectra.

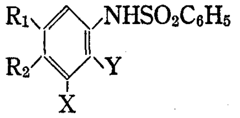
The reaction starting from *trans-p*-methoxypropenylbenzene (Ic) afforded 1-benzenesulfonamido-2-bromo-1-(4′-methoxyphenyl)propane (IIIc), colorless crystals, mp 91.5—92.5°, as the main product in the molar ratio of 1: 0.5 and 1: 1 (Ic: II). When reacted in a molar ratio of 1: 2 (Ic: II), bromo-substituted compound (IVc), mp 137—138°, and an oily product (VIII), considered to be 2-bromo-1-(3′-bromo-4′-methoxyphenyl)-1-propanol from its IR, NMR, and mass spectra, and VI were obtained.

When *trans-m*-methoxypropenylbenzene (Id) was reacted with II in a molar ratio of 1: 0.5 (Id: II), 1-benzenesulfonamido-2-bromo-1-(3′-methoxyphenyl)propane (IIId), mp 76—77.5°, was obtained as the main product, and the bromo-substituted compound (IVd),

Table II. Physical Constants and Elemental Analysis of the Products



Compd. No.	R_1	R_2	X	Y	mp (°C) (Recrystn. solvent)	IR (cm^{-1}) ν_{N-H}	Analysis (%) Calcd. (Found) C	H	N
IIIb	H	H	H	H	120—121 (EtOH)	3280	50.85 (50.65)	4.55 (4.75)	3.95 (3.93)
IIIc	H	OMe	H	H	91.5—92.5 (EtOH)	3275	49.98 (49.79)	4.72 (4.64)	3.65 (3.68)
IIId	OMe	H	H	H	76.0—77.5 (hexane–$CHCl_3$)	3250	48.86 (48.98)	4.87 (4.82)	3.56[a] (3.72)
IIIe	OMe	OMe	H	H	117.5—118.5 (EtOH)	3270	49.26 (49.39)	4.87 (4.78)	3.38 (3.35)
IVc	H	OMe	Br	H	137—138 (EtOH)	3250	41.49 (41.27)	3.70 (3.74)	3.02 (3.22)
IVd	OMe	H	H	Br	126—127.5 (MeOH–H_2O)	3275	41.49 (41.38)	3.70 (3.56)	3.02 (2.67)
IVe	OMe	OMe	H	Br	140—141 (EtOH)	3280	41.38 (41.49)	3.88 (3.84)	2.84 (2.95)
IVf	OMe	OBz	H	Br	166—167.5 (benzene)	3300	48.52 (48.60)	4.07 (4.14)	2.46 (2.19)



Compd. No.	R_1	R_2	X	Y	mp (°C) (Recrystn. solvent)	IR (cm^{-1}) ν_{N-H}	Analysis (%) Calcd. (Found) C	H	N
Ve	OMe	OMe	H	Br	154—155 (EtOH)	3275	45.15 (45.17)	3.79 (3.80)	3.76 (3.78)
V′e	OMe	OMe	H	H	129—130.5 (CH_2Cl_2)	3250	57.32 (57.20)	5.15 (5.11)	4.78 (4.64)
Vf	OMe	OBz	H	Br	133—134 (EtOH)	3275	53.58 (53.60)	4.05 (4.12)	3.12 (3.03)

a) Analysis Calcd. for $C_{16}H_{18}O_3NSBr \cdot 1/2H_2O$

mp 126—127.5°, in a molar ratio of 1: 2 (Id: II). A viscous liquid was obtained, when reacted in a molar ratio of 1: 1 (Id: II). Its NMR spectral data showed that it was a mixture of IIId and IVd. The separation of the components by silica gel column chromatography was unsuccessful, but the ratio of IIId and IVd was calculated as about 1: 2 by comparison of the areas of the peaks by integration of the NMR spectrum.

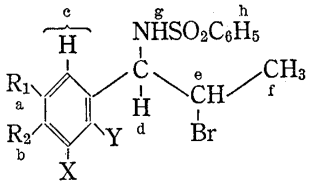
IVc was thought to be a 3′-bromo-substituted analog of IIIc on the basis of the coupling constants of peaks for three aromatic protons (Ha, Hb, Hc), as shown in Fig. 1 and Table III. Similarly, IVd was found to be a 6′-bromo-substituted analog of IIId, as shown in Fig. 2 and Table III.

No side-chain eliminated compound was observed, but general addition products (IIIb, c, d; IVc, d) were obtained in satisfactory yields, in these reactions starting from Ib, Ic, and Id, respectively. These facts suggest that the elimination may occur in the case of reactions starting from 3,4-dialkoxypropenylbenzene.

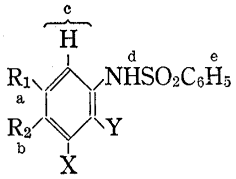
Therefore *trans*-3,4-dimethoxypropenylbenzene (Ie) which was purified by recrystallization from hexane, was reacted with DBBS (II) in the same way. When reacted in 1: 0.75 ratio, an addition product, 1-benzenesulfonamido-2-bromo-1-(3′,4′-dimethoxyphenyl)propane

(IIIe), was obtained, as colorless crystals, mp 117.5—118.5°. When reacted in 1:1 ratio, 6'-bromo-substituted analog of IIIe (IVe), colorless crystals, mp 140—141°, $C_{14}H_{15}O_4NS$ (V'e), mp 129—130.5°, and $C_{14}H_{14}O_4NSBr$ (Ve), mp 154—155°, were obtained. In the case of 1:1.5 ratio, the above product (V'e) was not obtained but IVe, Ve, and a small amount of a compound (IX), mp 239—240°, were formed. The structure of IX could not determined.

TABLE III. NMR Data of the Products[a]



	Ha	Hb	Hc	Hd	He	Hf	Hg	Hh
IIIb	—	—	7.10 (5H, s)	4.20—4.64 (2H, m)		1.57 (3H, d) J=6.5	5.83 (1H, d) J=8.5	7.20—7.76 (5H, m)
IIIc	—	3.73 (3H, s)	7.80 (4H, AB-qualtet) J=9.0	4.17—4.58 (2H, m)		1.55 (3H, d) J=6.0	5.75 (1H, d) J=8.5	7.30—7.77 (5H, m)
IIId	3.65 (3H, s)	—	6.54—7.08 (4H, m)	4.33—4.63 (2H, m)		1.56 (3H, d) J=6.5	5.96 (1H, d) J=8.0	7.20—7.77 (5H, m)
IIIe	3.70 (3H, s)	3.80 (3H, s)	6.61 (3H, s)	4.24—4.63 (2H, m)		1.56 (3H, d) J=6.5	5.88 (1H, d) J=8.0	7.23—7.80 (5H, m)
IVc	—	3.81 (3H, s)	6.60—7.30[b] (3H, m)	4.22—4.60 (2H, m)		1.56 (3H, d) J=6.0	5.66 (1H, d) J=7.5	7.33—7.78 (5H, m)
IVd	3.66 (3H, s)	—	6.46—7.30[c] (3H, m)	5.00 (1H, m)	4.45 (1H, m)	1.59 (3H, d) J=6.5	5.89 (1H, d) J=9.0	7.20—7.80 (5H, m)
IVe	3.74 (3H, s)	3.82 (3H, s)	6.83 (2H, s)	5.02 (1H, m)	4.48 (1H, m)	1.59 (3H, d) J=6.5	6.05 (1H, d) J=8.5	7.24—7.86 (5H, m)
IVf	3.72 (3H, s)	5.03 (2H, s) 7.35 (5H, s)	6.78 (1H, s) 6.88 (1H, s)	4.98 (1H, m)	4.47 (1H, m)	1.58 (3H, d) J=7.0	5.80 (1H, d) J=8.0	7.20—7.80 (5H, m)



	Ha	Hb	Hc	Hd	He
Ve	3.80 (3H, s)	3.89 (3H, s)	6.80 (1H, s) 7.25 (1H, s)	6.70 (1H, s)	7.34—7.80 (5H, m)
V'e	3.74 (3H, s)	3.80 (3H, s)	6.66 (3H, m)	6.90 (1H, s)	7.38—7.86 (5H, m)
Vf	3.88 (3H, s)	5.00 (2H, s) 7.32 (5H, s)	6.85 (1H, s) 7.25 (1H, s)	6.64 (1H, s)	7.30—7.80 (5H, m)

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a) Chemical shifts are given in ppm from $Si(Me)_4$ as an internal standard and coupling constant (J) in Hz.

b) *cf.* Fig. 1

c) *cf.* Fig. 2

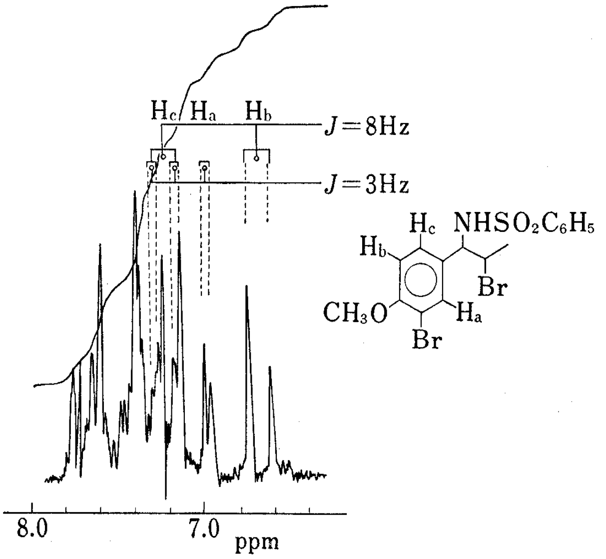

Fig. 1. NMR Spectrum of IVc

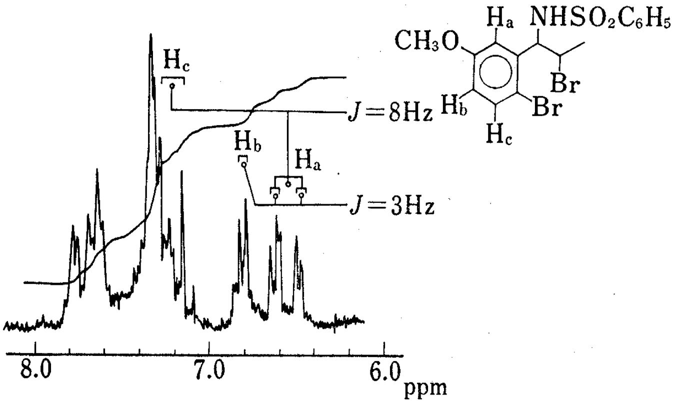

Fig. 2. NMR Spectrum of IVd

The compounds V′e and Ve showed the presence of NH in their IR spectra, and their NMR spectra exhibited no signals derived from the protons of C_3 fragment (Table III). The product V′e was identified by a mixed melting point determination and IR and NMR spectral comparisons with N-benzenesulfonyl-3,4-dimethoxyaniline, synthesized by the reaction of 3,4-dimethoxyaniline⁵⁾ with benzenesulfonyl chloride in alkaline solution, and Ve was similarly established as N-benzenesulfonyl-6-bromo-3,4-dimethoxyaniline synthesized by the reaction of V′e with bromine in acetic acid solution.

In order to investigate the substituted position of benzenesulfonamido group, *trans*-4-benzyloxy-3-methoxypropenylbenzene⁶⁾ (If) was reacted with DBBS in the same manner as above.

In each case starting from If, colorless crystals (IVf), mp 166—167.5°, and $C_{20}H_{18}O_4NSBr$ (Vf), mp 133—134°, were obtained as the main products. The structure of IVf was found to be 1-benzenesulfonamido-2-bromo-1-(4′-benzyloxy-6′-bromo-3′-methoxyphenyl)propane from its NMR spectral data (Table III). Vf was identified with N-benzenesulfonyl-4-benzyloxy-6-bromo-3-methoxyaniline synthesized by the bromination of N-benzenesulfonyl-4-benzyloxy-3-methoxyaniline (V′f), which was obtained by the reaction of 4-benzyloxy-3-methoxyaniline⁷⁾ with benzenesulfonyl chloride in alkaline solution.

In the reaction starting from Ia, Ie, and If, in which elimination reaction occurred, addition of 0.75 mol of DBBS to 1 mol of Ia, Ie, or If, color of the reaction solution changed rapidly from orange to pale yellow, and during these reactions gaseous HBr evolved vigorously, but in the reactions starting from Ib, Ic, or Id, such color change of the solution was not recognized, and gaseous HBr did not evolve in almost all cases.

With respect to the elimination of C_3 fragment, the above results indicate that (i) the elimination occurrs in the case of the molar ratio of I: II of less than 1: 1, and (ii) it occurrs only in the reaction starting from 3,4-dialkoxypropenylbenzene. Futhermore, according to the structure of the elimination product Vf, sulfonamido group was substituted in the position from which C_3 fragment was eliminated. The eliminated C_3 fragment could not be identified from the reaction mixture in this work, but this is being examined and will be reported at a later date.

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5) E.P. Clark, *J. Am. Chem. Soc.*, **53**, 3434 (1931).

6) F.J. Pond and F.T. Beers, *J. Am. Chem. Soc.*, **19**, 828 (1897).

7) J. Allan and R. Robinson, *J. Chem. Soc.*, **1926**, 376; N,L. Drake, H.C. Harris, and C.B. Jaeger, *J.Am. Chem. Soc.*, **70**, 168 (1948); F.S.H. Head, and A. Robertson, *J. Chem. Soc.*, **1931**, **1241**.

Experimental[8]

General Procedure——N,N-Dibromobenzenesulfonamide (II) was added to the stirred and cooled solution of propenylbenzene derivatives (Ib—f) in CH_2Cl_2, the reaction mixture was then stirred for 1 hr and refluxed for 2 hr. The solution was stirred with 10% aqueous $NaHSO_3$ for 1 hr and the separated CH_2Cl_2 layer was dried over $MgSO_4$. Evaporation of the solvent *in vacuo* left a syrupy residue. This residue was chromatographed on a silica gel column with CCl_4, CCl_4-$CHCl_3$ (9: 1, 8: 2), $CHCl_3$, and acetone. The isolated products were purified by recrystallization.

Reaction of Ib with II in 1: 1 Ratio——Ib (2.36 g, 0.02 mol) was allowed to react with II (6.30 g, 0.02 mol) in CH_2Cl_2 (30 ml) by the general procedure, and gave IIIb (5.99 g), VII (0.25 g, 4.5%), mp 58—60° (EtOH) (reported[9] mp 66—66.5°), NMR ($CDCl_3$) δ: 2.05 (3H, d, J=6.0 Hz, -CH_3), 4.47—4.82 (1H, m, -CHBr-Me), 5.06 (1H, d, J=10 Hz, -CHBr-), 7.35 (5H, s, -C_6H_5); Mass Spectrum m/e: 276/278/280 (M^+, 1: 2: 1), 197/199 (M^+-Br, 1: 1), 169/171 ($M^+-CHBrCH_3$, 1: 1), 118 (M^+-2Br); and VI (trace).

Reaction of Ib with II in 1: 1.5 Ratio——Ib (2.36 g, 0.02 mol) was reacted with II (9.45 g, 0.03 mol) in CH_2Cl_2 (30 ml). During this reaction, gaseous HBr did not evolve and the solution changed from pale yellow to red step by step. IIIb (5.33 g), VII (0.25 g, 4.5%), and VI (1.21 g) were obtained.

Reaction of Ic with II in 1: 0.5 Ratio——Ic (2.22 g, 0.015 mol) was reacted with II (2.37 g, 0.0075 mol) in CH_2Cl_2 (30 ml) by the same procedure. A part of IIIc (0.88 g) crystallized from the syrupy residue by treatment with hexane–$CHCl_3$. After removal of IIIc, residual oil (3.28 g) was chromatographed on a silica gel column. IIIc (1.44 g) and unstable oily product (1.20 g) which was found to be a mixture of several components from thin-layer chromatography (TLC), were eluted from the column.

Reaction of Ic with II in 1: 1 Ratio——Ic (1.48 g, 0.01 mol) was allowed to react with II (3.15 g, 0.01 mol) in CH_2Cl_2 (30 ml). During this reaction, gaseous HBr did not evolve. Removal of the solvent left a crystalline residue (3.93 g). From this residue, IIIc (3.09 g), unstable oily products (small amount), and VI (trace) were isolated by chromatography.

Reaction of Ic with II in 1: 2 Ratio——Ic (1.48 g, 0.01 mol) was reacted with II (6.3 g, 0.02 mol) in CH_2Cl_2 (20 ml). During this reaction gaseous HBr evolved, and formation of Br_2 was observed. During the treatment by general procedure, a part of VI (1.66 g) precipitated from the reaction mixture before being chromatographed. The first eluate contained an oily product (VIII) (0.26 g, 8.0%), IR ν_{max}^{Nujol} cm^{-1}: 3500 (OH); NMR ($CDCl_3$) δ: 1.55 (3H, d, J=6.5 Hz, -CH_3), 2.76 (1H, s, -OH), 3.86 (3H, s, -OCH_3), 4.35 (1H, m, -CHBr-), 4.85 (1H, d, J=4.5 Hz, -CH-), 6.84 (1H, d, J=8 Hz, arom.), 7.23 (1H, d-d, J=8 Hz, 2.5 Hz, arom.), 7.52 (1H, d, J=2.5 Hz, arom.); Mass Spectrum m/e: 322/324/326 (M^+, 1: 2: 1), 242/244 (M^+-HBr, 1: 1), 215/217 ($M^+-CHBrCH_3$, 1: 1), 199/201 ($M^+-OH-CHBrCH_3+H$, 1: 1), 164 (M^+-2Br). The second eluate contained IVc (3.67 g). The final eluate contained VI (0.18 g).

Reaction of Id with II in 1: 0.5 Ratio——Id (2.22 g, 0.015 mol) was reacted with II (2.36 g, 0.0075 mol) in CH_2Cl_2 (20 ml). Evaporation of the solvent left a syrupy residue (4.44 g) and it was chromatographed. The first eluate contained unstable oily product (1.18 g), which was a mixture of several components from the result of gas chromatography. The second fraction contained viscous oil (IIId) (2.35 g), which solidified from dil. MeOH. The final eluate contained a trace of VI.

Reaction of Id with II in 1: 1 Ratio——Id (1.48 g, 0.01 mol) was allowed to react with II (3.15 g, 0.01 mol) in CH_2Cl_2 (20 ml). During this reaction gaseous HBr and Br_2 were not detected. Residual oil (4.5 g) was obtained and chromatographed.

The first eluate contained unstable oily product (1.15 g), which was a mixture of several components from the result of gas chromatography. The second fraction (3.18 g) contained a mixture of IIId and IVd. The ratio of the components was judged to be 1: 2 from the NMR spectrum. The final eluate contained a trace of VI

Reaction of Id with II in 1: 1.5 Ratio——Id (1.48 g, 0.01 mol) was reacted with II (4.73 g, 0.015 mol) in CH_2Cl_2 (20 ml). During this reaction gaseous HBr and Br_2 did not evolve. Evaporation of the solvent left a syrupy residue containing crystals (5.54 g). When CCl_4 was added to the syrup, VI (0.67 g) was isolated. A viscous oil (VId) (3.49 g), giving one spot on the TLC, solidified from MeOH–hexane.

Reaction of Ie with II in 1: 0.75 Ratio——Ie[10] (2.67 g, 0.015 mol) was reacted with II (3.54 g, 0.011 mol) in CH_2Cl_2 (20 ml). A syrupy residue (6.18 g) was obtained. When ether was added to the syrup, IIIe (3.51 g) separated out which was separated by filtration and residual oil (2.4 g) was chromatographed. The first

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[8] All melting points are uncorrected. IR spectra were determined with Shimadzu IR-400 spectrophotometer, NMR spectra on Hitachi Perkin-Elmer R-20B spectrometer at 60 MHz in $CDCl_3$ with tetramethylsilane as internal standard, and mass spectra were recorded with a Shimadzu LKB-9000 mass spectrometer with an accelerating potential of 3.5 kV, an ionizing potential of 20 and 70 eV, and an ion source temperature of 230°.

[9] R.C. Huston and D.D. Sager, *J. Am. Chem. Soc.*, **48**, 1957 (1926).

[10] E. Funakubo, *Nippon Kagaku Zasshi*, **63**, 1628 (1942).

eluate (1.48 g) contained unstable compounds giving several spots on the TLC. The second eluate contained a part of IIIe (0.68 g). The final eluate contained a trace of VI.

Reaction of Ie with II in 1 : 1 Ratio——Ie (1.78 g, 0.01 mol) was allowed to react with II (3.15 g, 0.01 mol) in CH_2Cl_2 (15 ml). During the addition of II, the reaction mixture changed from initial yellow to orange, to pale yellow, and at the end to red. Gaseous HBr evolved when the solution was refluxed on a water bath. Evaporation of the solvent *in vacuo* left a brown syrupy residue (4.76 g). When ether was added to the syrup, a part of IVe (1.5 g) was obtained. Residual oil (3.26 g) was chromatographed, and Ve (0.69 g), IVe (1.61 g), V'e (0.41 g), and VI (trace) were eluted.

Reaction of Ie with II in 1 : 1.5 Ratio——Ie (1.78 g, 0.01 mol) was reacted with II (4.73 g, 0.015 mol) in CH_2Cl_2 (15 ml). The addition of a part of II (2.37 g) changed color of the solution from orange to pale yellow, and another addition of II changed it pale yellow to deep red. During refluxing of the solution on a water bath, gaseous HBr evolved vigorously and a part of VI precipitated. Evaporation of the solvent left a derk brown syrup (6.44 g), which was chromatographed. The first eluate was a trace of oil. The second contained Ve (0.88 g). The third contained IVe (3.61 g) and a small amount of IX, mp 239—240° (acetone). IR ν_{max}^{Nujol} cm^{-1}: 3250 (NH), 1340, 1150 (SO_2N). IX gave a positive Beilstein test. The final eluate contained VI (0.89 g).

Reaction of If with II in 1 : 1 Ratio——If[6)] (2.54 g, 0.01 mol) was reacted with II (3.15 g, 0.01 mol) in CH_2Cl_2 (15 ml). During this reaction, step by step, the solution turned yellow, orange, red, pale yellow, and finally red. Gaseous HBr evolved vigorously while the solution was refluxed. Evaporation of the solvent left a yellow brown solid (5.56 g). From which, Vf (0.37 g) and IVf (4.88 g) were isolated by chromatography.

Reaction of If with II in 1 : 1.5 Ratio——If (2.54 g, 0.01 mol) was reacted with II (4.73 g, 0.015 mol) in CH_2Cl_2 (20 ml). During this reaction, color of the solution changed similarly as in the above reaction. Gaseous HBr evolved vigorously while the solution was refluxed, and a part of VI precipitated. Evaporation of the solvent left a dark brown syrup (7.21 g). When ether was added to the syrup, a part of IVf (1.89 g) separated out which was separated by filtration. From the filtrate, Vf (1.37 g), IVf (2.54 g), and VI (0.82 g) were isolated by chromatography.

Synthesis of V'e and Ve——Benzenesulfonyl chloride (1.2 g) was added dropwise to a mixture of 3,4-dimethoxyaniline[5)] (0.2 g), acetone (trace), H_2O (10 ml), and 10% aqueous NaOH (2 ml) with stirring and ice-cooling. The stirring was continued for 2 hr, the mixture was extracted with $CHCl_3$, and the H_2O layer was acidified with dil. HCl. The acidic solution was extracted with $CHCl_3$. The organic layer was washed with H_2O, dried over $MgSO_4$, and evaporated to leave an oil (0.14 g), which solidified by treatment with ether, and recrystallized from CH_2Cl_2, mp 129—130.5°. These crystals were identified with V'e which was obtained from the reaction of Ie with II, by the mixed melting point determination and the comparison of IR and NMR spectra.

A solution of Br_2 (0.8 g) in AcOH (3 ml) was added to the stirred and ice-cooled solution of V'e (0.09 g) in AcOH (5 ml). Crystals (0.04 g) that precipitated were collected by filtration, and recrystallized from EtOH, mp 154—155°. These crystals were identified with Ve, by the mixed melting point determination and the comparisons of IR and NMR spectra.

Synthesis of Vf——Benzenesulfonyl chloride (4.05 g) was added dropwise to a mixture of 4-benzyloxy-3-methoxyaniline[7)] (1.08 g), acetone (trace), H_2O (50 ml), and 10% aqueous NaOH (14 ml) with stirring and ice-cooling. Stirring was continued for 1.5 hr. The solution was acidified with dil. HCl and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with 10% aqueous Na_2CO_3 and H_2O, dried over $MgSO_4$, and evaporated to leave an oil (1.32 g). The oil, N-benzenesulfonyl-4-benzyloxy-3-methoxyaniline (V'f), solidified by treatment with ether, and recrystallized from EtOH, mp 127.5—128.5°. IR ν_{max}^{Nujol} cm^{-1}: 3270 (NH), 1360, 1140 (SO_2N); NMR ($CDCl_3$) δ: 3.74 (3H, s, $-OCH_3$), 5.02 (2H, s, $-OCH_2Ph$), 6.35—6.77 (3H, m, arom.), 6.92 (1H, s, NH), 7.22—7.80 (10H, m, $-SO_2C_6H_5$, $-CH_2C_6H_5$). *Anal.* Calcd. for $C_{20}H_{19}O_4NS$: C, 65.2; H, 5.18; N, 3.79. Found: C, 65.21; H, 5.38; N, 3.68,

A solution of Br_2 (0.36 g) in AcOH (10 ml) was added to the stirred and ice-cooled solution of V'f (0.68 g) in AcOH (20 ml). Stirring was continued for 1 hr. The precipitated crystals (0.80 g) were collected by filtration and recrystallized from EtOH, mp 133—134°. The crystals were identified with Vf by the mixed melting point determination and the comparison of IR and NMR spectra.