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166. Shoji Takemura, Hiromi Terauchi, Yoshiko Ando, and Yoshio Ueno : Reaction of DL-*trans*- and DL-*cis*-2-Halo-1-benzenesulfonamidocyclohexanes. Formation and the Reaction of N-Benzenesulfonylcyclohexenimine.*1

(*Faculty of Pharmacy, Kinki University**2)

DL-*trans*-2-Halo-1-benzenesulfonamidocyclohexane (II) reacted with base such as silver acetate in benzene, cold sodium ethoxide, or cold ethanolic potassium hydroxide affording *meso-cis*-N-benzenesulfonylcyclohexenimine (I). The ring opening of I occurred by the action of hot ethanolic potassium hydroxide, hot sodium ethoxide, sodium hydrosulfide, acetic acid or hydrogen halides to form 2-substituted *trans*-1-benzenesulfonamidocyclohexanes (III, V, VI, IV, and II, respectively). Action of silver acetate on II in acetic acid afforded IV. Contrary to the reactions of II, the *cis* isomer (VII) did not form an imine ring.

An equilibrium was effected between I and II in the presence of a small amount of alkali, and heating of I with excess of mineral salts such as potassium halide and sodium halide, gave II.

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Our previous report*3 revealed that N,N-dihalobenzenesulfonamide reacts with cyclo-

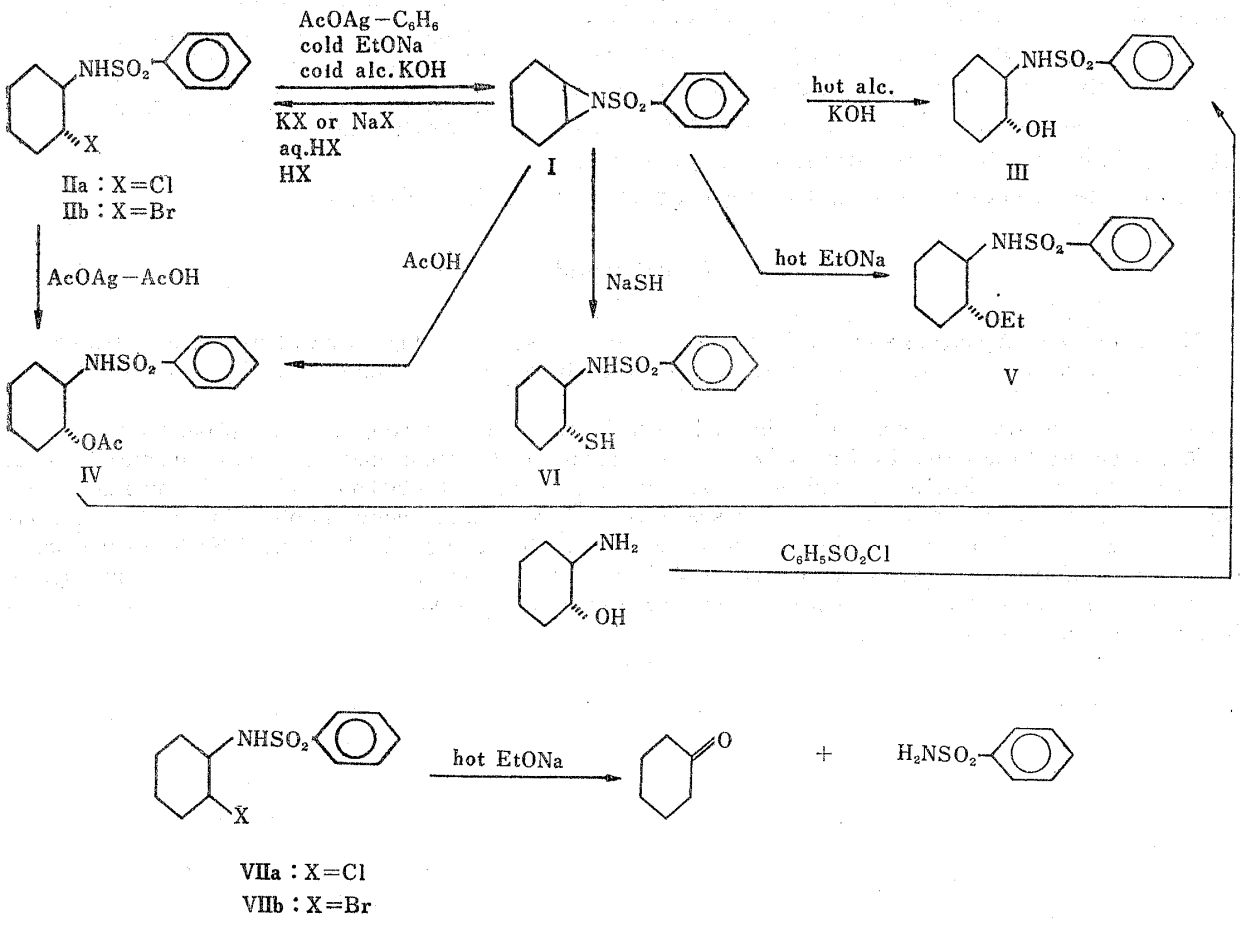


Chart 1.

*1 A part of this work was presented at the 85th Annual Meeting of the Pharmaceutical Society of Japan, Tokushima, October, 1965.

*2 Kowakae, Fuse, Osaka-fu (竹村庄司，寺内弘実，安藤佳子，上農義雄).

*3 This Bulletin, **15**, 1193 (1967).

hexene, undergoing characteristic addition to afford DL-*trans*-2-halo-1-benzenesulfonamidocyclohexane (II) and its *cis* isomer (VII) as major products.

During the course of the investigation on the structure and properties of II and VII, it became increasingly necessary to study the reaction of these substances in more details.

The reactions of II with some bases such as alkali hydroxide and ethoxide readily gave *meso-cis*-N-benzenesulfonylcyclohexenimine (7-benzenesulfonyl-7-azabicyclo[4.1.0]-heptane) (I). The imine ring of I was further cleaved by the action of the bases under relatively drastic conditions to give the corresponding 2-substituted DL-*trans*-1-benzenesulfonamidocyclohexanes. The opening of the imine ring also occurred readily by the action of acids such as hydrogen halide and acetic acid. On the other hand, it is of further interest that when I was refluxed in alkaline dioxane-water containing neutral mineral salts such as sodium chloride or potassium bromide, cleavage of C–N bond of the imine ring occurred to form II. Contrary to this, the corresponding *cis* isomer (VII) did not show such a behavior to the bases but was decomposed on heating for longer period.

DL-*trans*-2-Bromo-1-benzenesulfonamidocyclohexane (IIb) was refluxed with silver acetate in benzene and gave an oil of $b.p_4$ 165~170°, $b.p_{0.01}$ 149~152°, m.p. 23~25°, $C_{12}H_{15}O_2NS$, whose infrared spectrum lacked the N-H bond and its nuclear magnetic resonance spectrum, shown in Fig. 1, was also reasonable to give a structure I for the resulting compound. The chemical shifts were assigned for signals around 2.23τ (multiplet) to aromatic five protons, at 6.97τ to two protons in the imine ring, and a complex signal in a higher field to eight protons on the cyclohexane ring. In view of these observations and the chemical behaviors as described below, it is conclusive that this oil has the structure I.

It was evident that cyclohexenimine can exist only in the *cis*-configulation and not in *trans*.[1)]

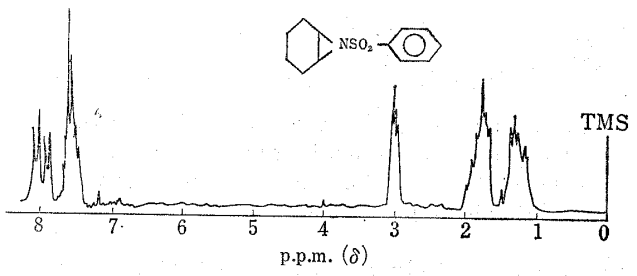


Fig. 1. Nuclear Magnetic Resonance Spectrum of *meso-cis*-N-Benzenesulfonylcyclohexenimine at 60 Mc. in Deuterochloroform

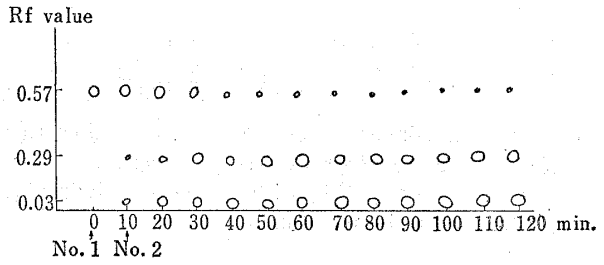


Fig. 2. Thin-layer Chromatogram of the Reaction Mixture of DL-*trans*-2-Bromo-1-benzenesulfonamidocyclohexane (IIb) with Potassium Hydroxide (1:1 molar ratio) in Ethanol

In addition to the cyclization of II with silver acetate, I was also formed by the action of II with cold ethanolic potassium hydroxide or cold sodium ethoxide in ethanol. Formation of I in these conditions was detected by a thin-layer chromatography. Further, when the cold solution of II in ethanolic potassium hydroxide was boiled, two spots identical with II and I as well as another spot were observed on the chromatogram. The compound corresponding to the latter spot was isolated from the reaction mixture by a column chromatography on silica gel as colorless crystals, m.p. 95~97°, $C_{12}H_{17}O_3NS$, which were identified with the authentic DL-*trans*-2-hydroxy-1-benzenesulfonamidocyclohexane (III). On refluxing in ethanolic solution of sodium ethoxide, II gave colorless crystals, m.p. 74~76°, $C_{14}H_{21}O_3NS$, which could presumably be given a structure of DL-

1) O. E. Paris, P. B. Fanta : J. Am. Chem. Soc., **74**, 3007 (1952).

trans-2-ethoxy-1-benzenesulfonamidocyclohexane (V). When II was heated with silver acetate in acetic acid, contrary to the case when heated in benzene, II gave an acetate, m.p. 108~111°, $C_{12}H_{15}O_2NS$, as tablets, whose infrared spectrum showed an absorption at 1720 cm^{-1}. The frequency is apparently assigned to that of acetate carbonyl. This acetate was identified as DL-*trans*-2-acetoxy-1-benzenesulfonamidocyclohexane (IV).

Probably the *trans*-substituted product-III or V-was formed from II through an intermediate (I) by an internal SN2 mechanism (Chart 1).

It is known[2] that aziridines easily react with various acids such as hydrogen halide to form addition products. The imine (X) also reacted with hydrogen chloride and bromide in ether or aqueous solution to give IIa and IIb, respectively. In a similar way, acetic acid reacted with I to form DL-*trans*-2-acetoxy-1-benzenesulfonamidocyclohexane (IV) which was identical with the authentic specimen.

On the formation of I from IIb by the action of ethanolic alkali, changes of contents in the reaction pathway were demonstrated by thin-layer chromatography. Fig. 2 illustrates the case in which the reaction was carried out in the presence of one equivalent potassium hydroxide. No. 1 shows the chromatogram of the solution immediately after mixing of IIb with I in cold ethanolic potassium hydroxide, where IIb is changed into the imine (I). When this mixture was refluxed for 10 min., two spots corresponding to IIb and III appeared on the chromatogram (No. 2); and after refluxing it for about 60 min., it seems that the ratio of contents (I, IIb, and III) is not changed any more.

Figs. 3 and 4 illustrate the chromatogram of the reaction mixtures in which 2 and 20 equivalent potassium hydroxide are used, respectively.

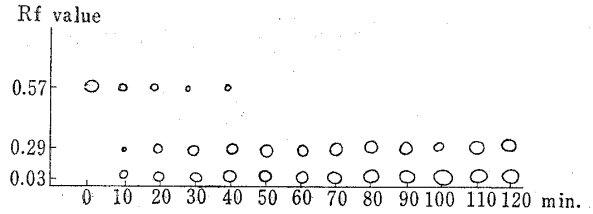


Fig. 3. Thin-layer Chromatogram of the Reaction Mixture of DL-*trans*-2-Bromo-1-benzenesulfonamidocyclohexane (IIb) with Potassium Hydroxide (1:2 molar ratio) in Ethanol

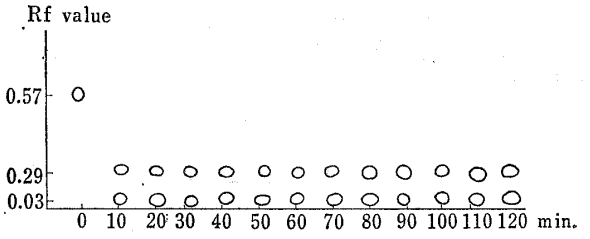
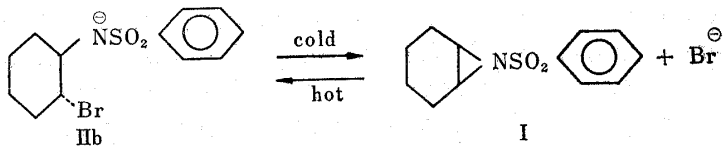


Fig. 4. Thin-layer Chromatogram of the Reaction Mixture of DL-*trans*-2-Bromo-1-benzenesulfonamidocyclohexane (IIb) with Potassium Hydroxide (1:20 molar ratio) in Ethanol

These results are sufficient to assume that an equilibrium may be effected between IIb and I; namely, in the cold condition, the equilibrium seems to be inclined toward I while somewhat toward IIb in the hot.



IIb I

This consideration led to a presumption that a large excess of potassium bromide in the hot condition would make the equilibrium incline toward IIb. Then the imine (I) was heated with excess potassium bromide in dioxane-water containing small amount

2) M. S. Kharasch, H. M. Priestley : J. Am. Chem. Soc., **61**, 3425 (1935); T. Taguchi, M. Kojima, T. Muro : *Ibid.*, **81**, 4322 (1959); T. Taguchi, M. Kojima : *Ibid.*, **81**, 4318 (1959); O. E. Paris, P. E. Fanta : *Ibid.*, **74**, 3003 (1952).

of potassium hydroxide and, as expected, considerable amount of IIb was isolated from the reaction mixture by column chromatography. In a similar manner, sodium chloride reacted with I to give IIa in a lower yield than in the case of potassium bromide. In addition, it was shown that similar reversible change was found to occur in a neutral medium.

These observations are of interest in comparison with the reaction of β-lactones[3] and sultones[4] with various mineral salts. More recently, Heine[5] and Fanta, *et al.*[6] reported on the reaction of N-acylazipidines with sodium iodide in acetone or acetonitrile to form iodo amides with ring cleavage.

In the present case, both the strong electron-attracting benzenesulfonyl group and the strain of a three-membered imine ring probably accelerate the cleavage of the C-N bond and cause the equilibrium.

Sodium hydrosulfide was reacted with I in ethanol and DL-*trans*-2-mercapto-1-benzenesulfonamidocyclohexane (V), m.p. 151~153°, $C_{12}H_{17}O_2NS_2$, was formed.

Experimental

***meso-cis*-N-Benzenesulfonylcyclohexenimine (I)**——A mixture of DL-*trans*-2-bromo-1-benzenesulfonamidocyclohexane (IIb) (10 g.), AcOAg (6.4 g.), and benzene (50 ml.) was refluxed for 3 hr. The precipitated AgBr was filtered off and the precipitate was washed with abs. benzene. The filtrate and washing were combined, evaporated to dryness *in vacuo*, and the residue was chromatographed on silica gel column. From the first eluate eluted with $CHCl_3$, an oil was obtained which was distilled under a reduced pressure, $b.p_{0.01}$ 149~152°, m.p. 23~25° (4.3 g.). *Anal.* Calcd. for $C_{12}H_{15}O_2NS$: C, 60.71; H, 6.37; N, 5.91. Found: C, 60.76; H, 6.44; N, 5.62. IR ν_{max}^{Nujol} cm^{-1}: 1320, 1155 (ν_{SO_2N}). NMR (Fig. 1).

Application of this procedure to the chloro analog (IIa) to obtain I failed.

DL-*trans*-2-Hydroxy-1-benzenesulfonamidocyclohexane (III)——i) From I: *meso-cis*-N-Benzenesulfonylcyclohexenimine (I) (121 mg.) was added to 5.6% KOH in 50% EtOH (5 ml.) and the mixture was refluxed for 2 hr. The solution was cooled, neutralized with AcOH (0.3 ml.), evaporated to remove EtOH, and H_2O was added to the residue. The mixture was extracted with $CHCl_3$, the $CHCl_3$ layer was washd with H_2O, and dried over anhyd. Na_2SO_4. It was evaporated to dryness and remained oil was treated with iso-$(C_3H_7)_2O$-acetone (3:2) by which the oil turned into a solid (40 mg.). It was recrystallized from iso-$(C_3H_7)_2O$-acetone (2:1) to colorless crystals, m.p. 95~97° (24 mg.). *Anal.* Calcd. for $C_{12}H_{17}O_3NS$: C, 56.43; H, 6.71; N, 5.49. Found: C, 56.71; H, 6.39; N, 5.17. IR ν_{max}^{Nujol} cm^{-1}: 3200~3560 ($\nu_{O-H,\ N-H}$), 1325, 1153 (ν_{-SO_2N}).

ii) Form IV: DL-*trans*-2-Acetoxy-1-benzenesulfonamidocyclohexane (IV) (1 g.) was added to 4% NaOH in EtOH (5 ml.) and the mixture was refluxed on a water bath for 3 hr. The reaction mixture was neutralized with AcOH (0.3 ml.) and the solution was evaporated to dryness *in vacuo*. Addition of H_2O and trituration made the residue solidify and the solid was recrystallized from iso-$(C_3H_7)_2O$-acetone (2:1) to colorless crystals, m.p. 95~97° (350 mg.). It was identical with the sample obtained from the method (i) by a mixed melting point determination.

iii) From DL-*trans*-2-Hydroxy-1-cyclohexylamine[1]: To a mixture of DL-*trans*-2-hydroxy-1-cyclohexylamine (5 g.) and NaOH (3.1 g.) in H_2O (100 ml.), $C_6H_5SO_2Cl$ (7.6 g.) was added dropwise under ice-cooling and stirring. The mixture was stirred for more 15 min. after the addition was completed. The resulting liquor was acidified with AcOH (3 ml.), extracted with $CHCl_3$ (60 ml.), the $CHCl_3$ layer was washed with H_2O, dried over Na_2SO_4, and the solution was evaporated to remove the solvent. The residue was dissolved in hot AcOEt (15 ml.) and refrigerated overnight to obtain colorless crystals, m.p. 95~97° (5.2 g.). These were identified with the authentic sample by a mixed fusion.

Formation of *meso-cis*-N-Benzenesulfonylcyclohexenimine (I) and DL-*trans*-2-Ethoxy-1-benzenesulfonamidocyclohexane (V) by the Action of Sodium Ethoxide to II——i) From IIa: DL-*trans*-2-Chloro-1-benzenesulfonamidocyclohexane (IIa) (1.4 g.) was added to 0.5*M* EtONa in EtOH (25 ml.). After standing at

3) J. L. Gresham, J. E. Jansen, F. W. Shaver, J. T. Gregory: J. Am. Chem. Soc., **70**, 999 (1948); H. B. Haao, H. Feuer, S. M. Pier: *Ibid.*, **73**, 1858 (1951); J. L. Gresham, *et al.*: *Ibid.*, **74**, 1323 (1952); J. L. Gresham: U. S. Pat., 2,449,987 (1948) (C. A., **43**, 1056 (1948)).

4) J. H. Helberger: Reichsant Wirshaftaufbau Chem. Br. Pruf. Nr. **15** (C. A., **41**, 4101 (1947)); J. H. Helberger, G. Manecke: Ger. Pat., 895,559 (1953) (C. A., **48**, 12792 (1954)).

5) H. W. Heine: Angew. Chem., **74**, 772 (1962).

6) P. E. Fanta, E. N. Walsh: J. Org. Chem., **30**, 3574 (1965).

room temperature for 20 min., the mixture was refluxed on a water bath for 1 hr. This solution was acidified with 10% HCl, extracted with two portions of $CHCl_3$ (15 ml.), and the $CHCl_3$ layer was dried over anhyd. Na_2SO_4. After removal of the solvent, the residue was chromatographed on a silica gel column. From the first fraction developed with $CHCl_3$ an oily residue (0.3 g.) was obtained which distilled at $b.p_{0.01}$ 149°. It was identical with the authentic I by comparison of IR spectra. The second fraction contained a yellow oily material which soon solidified on cooling. Recrystallization of it from iso-$(C_3H_7)_2O$ gave colorless prisms, m.p. 75° (0.3 g.), which were identified with the authentic DL-*trans*-2-ethoxy-1-benzenesulfonamidocyclohexane (V) by comparison of IR spectra and by a mixed fusion.

ii) From IIb: DL-*trans*-2-Bromo-1-benzenesulfonamidocyclohexane (IIb) (3 g.) was added to EtONa solution prepared by dissolving Na (0.2 g.) in abs. EtOH (30 ml.). The mixture was stirred until IIb dissolved, refluxed at 95° for 2 hr., and evaporated *in vacuo*. The residue was added to H_2O (15 ml.), acidified by addition of 3.5% HCl, and extracted with two portions of $CHCl_3$ (10 ml.). The $CHCl_3$ layer was washed with H_2O, dried over Na_2SO_4, and evaporated to give a yellow oil, which was chromatographed on a silica gel column. From the first fraction developed with *n*-hexane–$CHCl_3$, an oil, $b.p_{0.01}$ 200° (bath-temperature) (0.43 g.), was obtained. It was identical with I by comparison of IR spectra and Rf values.

The second fraction was distilled to obtain an oil, $b.p_{0.01}$ 210° (bath-temperature). The solidified oil (1 g.) was recrystallized from iso-$(C_3H_7)_2O$ to V as colorless prisms, m.p. 74~76° (800 mg.). *Anal.* Calcd. for $C_{14}H_{21}O_3NS$: C, 59.33; H, 7.47; N, 4.95. Found: C, 59.20; H, 7.29; N, 4.83. IR ν_{max}^{Nujol} cm^{-1}: 3300 (ν_{N-H}), 1325, 1166 (ν_{-SO_2N}).

Final elution of the column with MeOH gave a small amount of a solid material. Recrystallization of it from iso-$(C_3H_7)_2O$–acetone afforded colorless crystals, m.p. 95~97°, which were identical with III by comparison of IR spectra and a mixed melting point determination.

DL-*trans*-2-Acetoxy-1-benzenesulfonamidocyclohexane (IV)——i) From IIb with AcOAg in AcOH: A mixture of DL-*trans*-2-bromo-1-benzenesulfonamidocyclohexane (IIb) (3.5 g.), AcOAg (3.5 g.), and AcOH (35 ml.) was refluxed in an oil bath for 3 hr. The precipitated AgBr was filtered off and it was washed with AcOH. The filtrate and washing were combined, evaporated to dryness *in vacuo*, and the residue was recrystallized from 95% EtOH to colorless crystals, m.p. 108~111° (1.5 g.). *Anal.* Calcd. for $C_{12}H_{15}O_2NS$: C, 56.56; H, 6.44; N, 4.71. Found: C, 56.68; H, 6.41; N, 4.46. IR ν_{max}^{Nujol} cm^{-1}: 3240 (ν_{N-H}), 1720 ($\nu_{C=O}$), 1331, 1162 (ν_{-SO_2N}).

ii) From I with AcOH: A mixture of *meso-cis*-N-benzenesulfonylcyclohexenimine (I) (2 g.) and AcOH (20 ml.) was refluxed in an oil bath for 3 hr. The solvent was evaporated *in vacuo* and the residue was recrystallized from 95% EtOH to colorless prisms, m.p. 107~109° (1.8 g.), whose mixed melting point with the authentic IV was not depressed.

Formation of IIa and IIb from I——i) Action of HCl on I: Dried HCl was bubbled through a solution of I (0.5 g.) in abs. Et_2O (10 ml.) until the separation of a solid was completed. The solid was collected by filtration and recrystallized from 95% EtOH to colorless needles, m.p. 156~159° (0.3 g.), and these were identified with the authentic sample by a mixed melting point determination.

ii) Action of HCl on I in Water: I (0.3 g.) was added to 10% HCl (7 ml.), and the mixture was refluxed for 2 hr. After cooled, the crystals were collected by suction and washed with H_2O. Recrystallization from MeOH gave colorless crystals, m.p. 156~158° (0.25 g.), which were identified with sample of IIa by a mixed fusion.

iii) Action of HBr on I: Dried HBr was bubbled through a solution of I (2.43 g.) in CCl_4 (20 ml.). After cooled, the separated crystals were collected by suction and recrystallized from EtOH to colorless needles, m.p. 160~164° (2.66 g.). These were identified with the authentic IIb by a mixed fusion.

iv) Action of HBr on I in Water: I (0.1 g.) was added to 10% aq. HBr (5 ml.) and the mixture was refluxed for 30 min. After cooled, the crystals were collected, and recrystallized from MeOH to colorless needles, m.p. 164~166° (0.12 g.), which were identified with the authentic IIb by a mixed melting point determination.

DL-*trans*-2-Mercapto-1-benzenesulfonamidocyclohexane (VI)——Na (0.94 g.) was dissolved in abs. EtOH (30 ml.) and the solution was saturated with dried H_2S under cooling. I (2 g.) was added to this solution and the mixture was refluxed in an oil bath for 1 hr. After cooled, the reaction mixture was acidified with AcOH (3 ml.) and evaporated to dryness *in vacuo*. The residue was dissolved in H_2O (30 ml.) and extracted with three portions of $CHCl_3$. The $CHCl_3$ layer was dried over Na_2SO_4 and the solvent was distilled off. The residue was chromatographed on a silica gel column to obtain colorless needles (150 mg.) which were recrystallized from MeOH, m.p. 151~153°. *Anal.* Calcd. for $C_{12}H_{17}O_2NS_2$: C, 53.13; H, 6.32; N, 5.16. Found: C, 53.23; H, 6.26; N, 5.35. IR ν_{max}^{Nujol} cm^{-1}: 3220 (ν_{N-H}), 1319, 1152 (ν_{-SO_2N}).

Thin-layer Chromatography[*4] during the Reaction of IIb and Ethanolic KOH——A solution of KOH (0.18 g., 0.003 mol.) in 50% aq. EtOH (10 ml.) was mixed with IIb (0.98 g., 0.003 mol.). The solid dissolved by stirring at room temperature and at the same time, a small amount of oily substance separated. The

[*4] Thin-layer chromatography was carried out with Silica Gel G (Merck) and developed with chloroform–cyclohexane–ethyl acetate (7:3:0.3).

thin-layer chromatogram of this solution and the oil showed only one spot at Rf 0.57 which was identical with that of I (Fig. 1, No. 1). The reaction mixture was then refluxed in an oil bath and, during the refluxing, the mixture was checked every 10 minutes by a thin-layer chromatography. Since the refluxing started, three spots were always detected at Rf 0.57, 0.29, and 0.03, which corresponded to I, IIb, and III, respectively. The proportional areas of the spots were unchanged after heating for 1 hr. After heating for 2 hr., the solution was acidified by adding conc. HCl (0.5 ml.), then the solvent was evaporated under a reduced pressure, the residue was mixed with H_2O (5 ml.), and the suspension was extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O, dried over Na_2SO_4, and evaporated to leave an oil, which was chromatographed on a silica gel column. Development with *n*-hexane–$CHCl_3$ (5:1) gave I, b.$p_{0.01}$ 149~150°, and that with $CHCl_3$, III, m.p. 95~97°. Identification of IIb and III was made by mixed melting points and comparison of IR spectra with the authentic samples. Experiments in increased concentrations of KOH (2 moles and 20 moles) are shown in Fig. 3 and 4. In both cases, it was found by chromatography that, immediately after refluxing of the mixture, I formed in cold rapidly changed to IIb and III.

Formation of IIb from I with KBr——I (0.98 g., 0.004 mol.) was added to a solution of KBr (2.38 g., 0.02 mol.) in aq. dioxane (50%) containing 2% KOH. The resulting solution was refluxed in an oil bath for 40 min. After cooled, the solution which was separated into two phases was acidified with conc. HCl (15 ml.), evaporated to dryness *in vacuo*, and the residue was mixed with H_2O. This mixture was extracted with $CHCl_3$, the $CHCl_3$ layer was washed with H_2O, dried over Na_2SO_4, and evaporated to obtain a solid crude mixture. This was chromatographed on a silica gel column. Elution with *n*-hexane–$CHCl_3$ (2:1) gave a crystalline product (44%), m.p. 159~163° (from EtOH), which was identified with IIb by showing no depression of mixed melting point with the authentic sample. IR spectrum and Rf value were also identical with IIb. Elution of the column with $CHCl_3$ resulted a crop of crystals as colorless plates, m.p. 95~98° (50%), which was identical with the authentic III by a mixed fusion and by comparison of IR spectra.

Experiment without addition of KOH under the same condition was carried out and the yields of IIb and III were 27% and 40%, respectively, the recoverly of I was 30%.

Formation of IIa from I with NaCl——NaCl (1.2 g., 0.02 mol.) was dissolved in a solution of NaOH (2%) in 50% aq. dioxane and I (1.03 g., 0.004 mol.) was added. The mixture was refluxed in an oil bath for 40 min. The solution, separated into two phases, was acidified with conc. HCl (15 ml.), evaporated to dryness *in vacuo*, and H_2O was added to the residue. The resulting suspension was extracted with $CHCl_3$, the $CHCl_3$ layer was washed with H_2O, dried over anhyd. Na_2SO_4, and the solvent was evaporated to leave a solid residue, which was chromatographed on a silica gel column to separate into two crystalline materials; one of them, m.p. 154~156°, was identical with the authentic IIa by a mixed fusion and another of m.p. 95~97° was identical with the sample of III by a mixed melting point determination.

Reaction of DL-*cis*-2-Chloro-1-benzenesulfonamidocyclohexane (VIIa) with NaOEt——A mixture of VIIa (1.47 g.) and 0.5*M* EtONa in EtOH (20 ml.) was refluxed for 32 hr. The reaction mixture was acidified with 10% HCl, evaporated to dryness *in vacuo*, and the residue was extracted with $CHCl_3$. After removal of the solvent from the extract, the residue was subjected to alumina chromatography. Elution of the column with $CHCl_3$ afforded benzenesulfonamide (0.3 g.) and recovered VIIa (0.5 g.).

In another run, the reaction mixture obtained by the same procedure was acidified with 10% HCl and the solution was distilled under a reduced pressure to collect 18 ml. of a distillate, which was treated with 2,4-dinitrophenylhydrazine to obtain a yellow hydrazone as needles, m.p. 160° (from EtOH). It was identified by comparison of IR spectra and a mixed fusion with 2,4-dinitrophenylhydrazone of cyclohexanone.

Reaction of DL-*cis*-2-Bromo-1-benzenesulfonamidocyclohexane (VIIb) with NaOEt——A mixture of VIIb (1 g.) and 0.3*M* EtONa in EtOH (30 ml.) was refluxed for 22 hr. The reaction mixture was acidified with 10% HCl and the solution was distilled under reduced pressure. About 20 ml. of distillate was collected which was treated with 2,4-dinitrophenylhydrazine to obtain yellow needles, m.p. 161°. It was identical with the authentic 2,4-dinitrophenylhydrazone of cyclohexanone by a mixed fusion.

The residue after the above distillation was extracted with $CHCl_3$, the extract was washed with H_2O, dried over Na_2SO_4, and the solvent was removed. The residue was chromatographed on an alumina column. Elution of the column with $CHCl_3$ gave recovered VIIb (0.1 g.) and the subsequent elution with $CHCl_3$–MeOH (10:1) gave benzenesulfonamide (0.3 g.).