

Studies on 3-Substituted 1,2-Benzisoxazole Derivatives. V.¹⁾ Electrophilic Substitutions of 1,2-Benzisoxazole-3-acetic Acid

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The site of the electrophilic substitution of 1,2-benzisoxazole-3-acetic acid (**1**) altered depending on species of electrophiles and reaction conditions. In halogenation, only the α -methylene group of **1** was substituted. In the chlorosulfonation, the α -methylene group was substituted at first and then the 5-position of the nucleus was substituted. On the other hand, in the nitration, the 5-position was substituted at first and the α -methylene group was substituted secondly.

Keywords—1,2-benzisoxazole; electrophilic substitution; chlorination; nitration; sulfonation; formylation

In the previous paper,³⁾ it was reported that α -methylene group of 1,2-benzisoxazole-3-acetic acid (**1**) is active to the electrophilic replacement and easily brominated to give α -bromo-1,2-benzisoxazole-3-acetic acid and 3-tribromomethyl-1,2-benzisoxazole. As an extension of this series, the present paper deals with some reactions of **1** with several electrophiles.

Chlorination of **1**

The chlorination of **1** with 1.1 molar equivalent of chlorine gave α -chloro-1,2-benzisoxazole-3-acetic acid (**2**) and 3-dichloromethyl-1,2-benzisoxazole (**3**), but 3-trichloromethyl-1,2-benzisoxazole (**4**) was not obtained. The compound **4** was obtained by the reaction of **1** with an excess of iodine monochloride (ICl) in carbontetrachloride, in 30% yield.

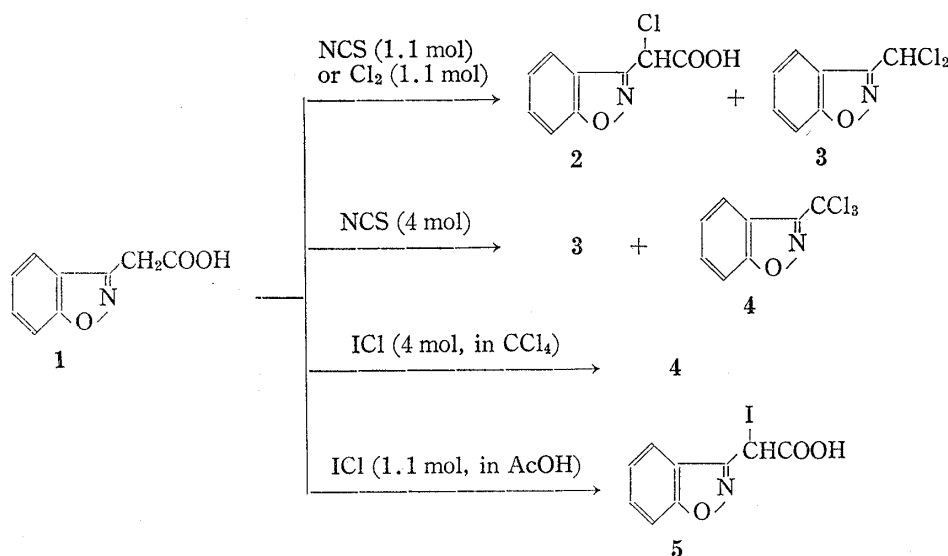


Chart 1

1) Part IV: H. Uno and M. Kurokawa, *Chem. Pharm. Bull.* (Tokyo), **26**, 549 (1978).

2) Location: 33-94, Enoki-cho, Suita, Osaka.

3) H. Uno, M. Kurokawa, K. Natsuka, Y. Yamato, and H. Nishimura, *Chem. Pharm. Bull.* (Tokyo), **24**, 632 (1976).

The chlorination of **1** with 1.1 molar equivalent of N-chlorosuccinimide (NCS) afforded a mixture of **2** and **3**. With 4 molar equivalent of NCS, **1** afforded an oily mixture of **3** and **4**.

On the other hand, the reaction of **1** with 1.1 molar equivalent of ICl in acetic acid gave α -iodo-1,2-benzisoxazole-3-acetic acid (**5**) in 14% yield.

Nitration of **1**

When **1** was reacted with fuming nitric acid ($d=1.5$) under cooling in an ice-bath for 1/2 hr, a mixture of three products (**6**, **7** and **8**) was obtained.

The infrared (IR) spectrum of **6**, $C_9H_6N_2O_5$, revealed an absorption band due to a carboxyl group at 1720 cm^{-1} . The nuclear magnetic resonance (NMR) spectrum of **6** revealed signals of two methylene protons at δ 4.27, one proton exchangeable with deuterium at δ 13.00 and three aromatic protons at δ 7.98 (doublet, $J=10\text{ Hz}$), 8.93 (doublet, $J=2\text{ Hz}$) and 8.53 (doublet, $J=2$ and 10 Hz). From these data **6** was determined to be 5-nitro-1,2-benzisoxazole-3-acetic acid.

The IR spectrum of **7**, $C_8H_4N_4O_7$, exhibited no absorption band due to a carbonyl group. The NMR spectrum of **7** revealed signals of three aromatic protons and a broad signal of a proton at δ 11.5. Based on these spectral data, the structure of **7** was assigned as 3-dinitro-methyl-5-nitro-1,2-benzisoxazole. The mass spectrum of **8**, $C_{16}H_6N_6O_8$, revealed the molecular ion (M^+) peak at m/e 410 and a strong $M^+/2$ fragment peak at m/e 205. It was suggested that **8** was a dimerized compound. The IR spectrum of **8** revealed no absorption band due to

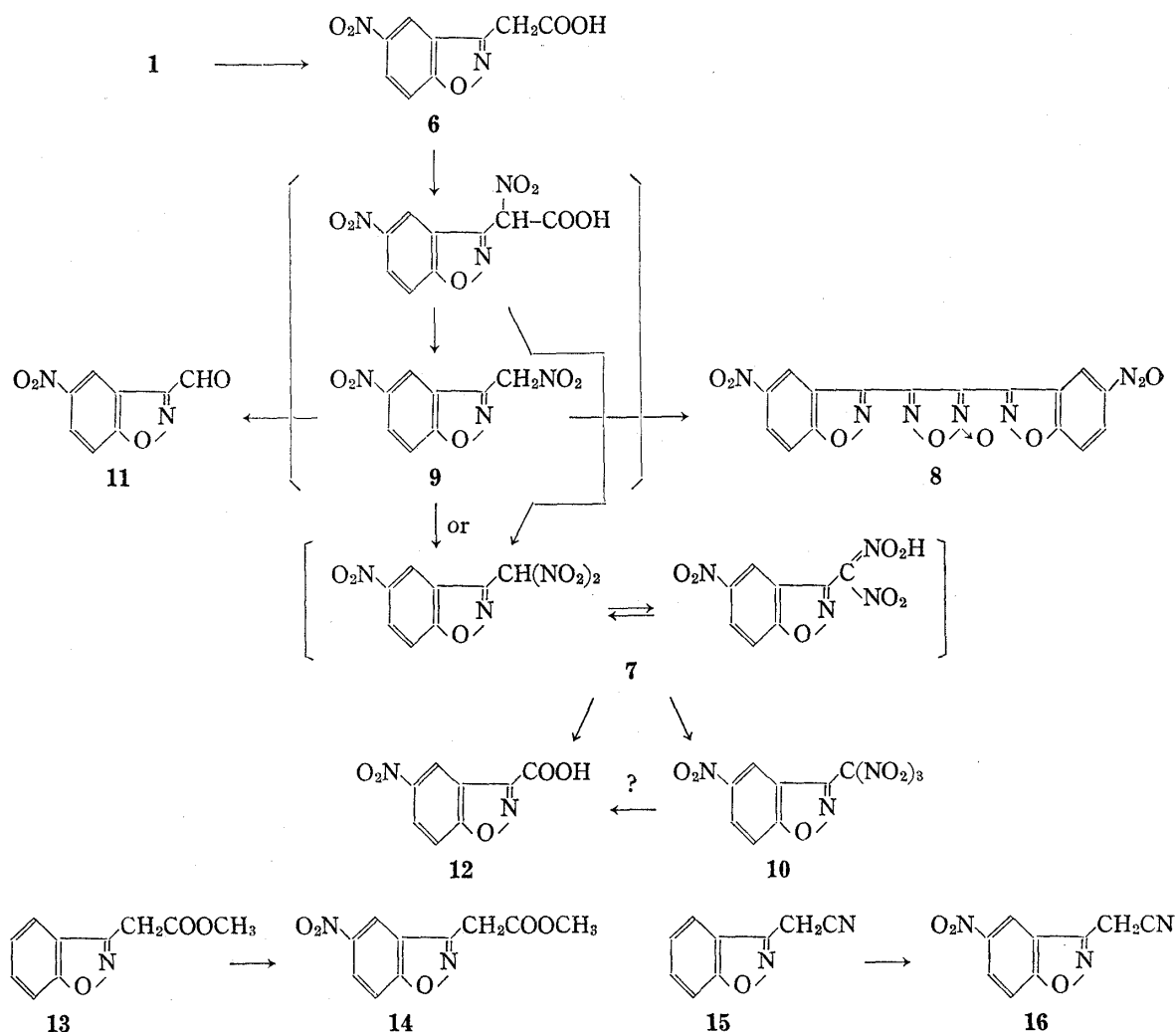


Chart 2

a carboxyl group. The NMR spectrum of **8** revealed signals of two pairs of aromatic protons (δ 9.12 and 8.98; 8.68 and 8.67) and a signal of two aromatic protons at δ 8.20. These facts suggested that **8** had an asymmetric structure. Thus the structure of **8** was assigned as bis-(5-nitro-1,2-benzisoxazol-3-yl)furoxan.

Snyder, *et al.*⁴⁾ reported that in the nitration of acetophenone, bisbenzoylfuroxan was formed *via* benzoylnitromethane. Therefore, the formation of **8** *via* 3-mononitromethyl-5-nitro-1,2-benzisoxazole (**9**) was suggested.

When **1** was treated with fuming nitric acid ($d=1.5$) under cooling in an ice-bath for 1 hr and then at room temperature for 2 hr, in addition to **7** and **8**, other three compounds (**10**, **11** and **12**) were obtained. The IR spectrum of **10**, $C_8H_3N_5O_9$, revealed no absorption band due to a carboxyl group and its NMR spectrum revealed signals of three aromatic protons but no signal of methylene proton. Thus the structure of **10** was assigned to be 5-nitro-3-(trinitromethyl)-1,2-benzisoxazole.

The IR spectrum of **11**, $C_8H_4N_2O_4$, showed an absorption band due to a carbonyl group at 1700 cm^{-1} . The NMR spectrum of **11** showed a signal due to a proton of aldehyde at δ 10.47. Therefore, **11** was assigned as 5-nitro-1,2-benzisoxazole-3-carboxaldehyde. The IR spectrum of **12**, $C_8H_4N_2O_5$, showed absorption bands due to a hydroxyl group at $3100\text{--}2500\text{ cm}^{-1}$, and a carboxyl group at 1710 and 1690 cm^{-1} . Thus **12** was assigned as 5-nitro-1,2-benzisoxazole-3-carboxylic acid. The hydrolysis of **10** with 90% sulfuric acid afforded **12**. Compound **12** was also obtained by the hydrolysis of tribromomethyl-1,2-benzisoxazole.³⁾

The nitration of **6** afforded **7**, **8**, **10**, **11** and **12**, and the nitration of **7** afforded **10** and **12**. The nitration of **1** may be summarized in Chart 2.

On the other hand, the nitration of methyl 1,2-benzisoxazole-3-acetate (**13**) afforded only methyl 5-nitro-1,2-benzisoxazole-3-acetate (**14**) in 50% yield. And the nitration of 1,2-benzisoxazole-3-acetonitrile (**15**) afforded 5-nitro-1,2-benzisoxazole-3-acetonitrile (**16**) in 90% yield.

Sulfonation of **1**

The chlorosulfonation of **1** with an excess of chlorosulfonic acid at 60° for 7 hr and the successive amination with 28% ammonium hydroxide, afforded a mixture of two products, **17** and **18**, in 17% and 4% yields, respectively.

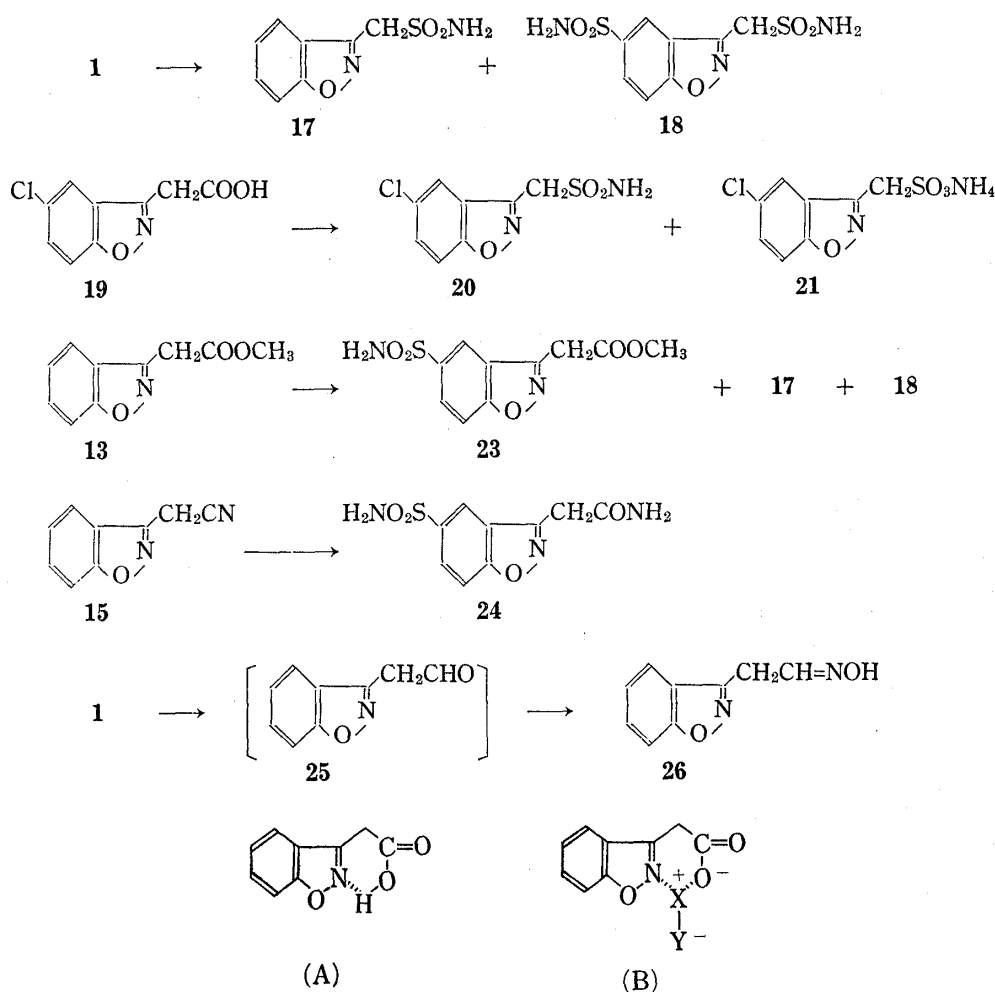
The IR spectrum of **17**, $C_8H_8N_2O_3S$, revealed no absorption band due to a carboxyl group and a hydroxyl group but bands due to an amino group at 3320 and 3160 cm^{-1} and a sulfonyl group at 1330 and 1145 cm^{-1} . The NMR spectrum of **17** revealed signals due to two methylene protons at δ 4.85. Therefore, **17** was assigned as 3-sulfamoylmethyl-1,2-benzisoxazole. The NMR spectrum of **18**, $C_8H_9N_3O_5S_2$, revealed two methylene protons at δ 4.93 and three aromatic protons at δ 7.97 (1H, double doublet, $J=1$ and 10 Hz), 8.17 (1H, double doublet, $J=2$ and 10 Hz) and 8.50 (1H, double doublet, $J=1$ and 2 Hz). Thus, **18** was assigned as 3-sulfamoylmethyl-5-sulfamoyl-1,2-benzisoxazole.

The chlorosulfonation and the successive amination of 5-chloro-1,2-benzisoxazole-3-acetic acid (**19**), in which 5-position was blocked with a chlorine atom, afforded 5-chloro-3-sulfamoylmethyl-1,2-benzisoxazole (**20**) and ammonium salt of 5-chloro-1,2-benzisoxazole-3-methanesulfonic acid (**21**) in 26% and 27% yields, respectively.

The sulfonation of **1** with a mixture of chlorosulfonic acid and dioxane in dichloromethane afforded 1,2-benzisoxazole-3-methanesulfonic acid (**22**) as a sole product, which was converted to its chloride with phosphorous oxychloride and then led to **17**. The melting point and spectral data of this compound were in good accordance with those of a sample obtained in the former reaction.

The chlorosulfonation and the successive amination of **13** afforded **17**, **18** and methyl 5-sulfamoyl-1,2-benzisoxazole-3-acetate (**23**). And the same reaction of 1,2-benzisoxazole-3-acetonitrile (**15**) afforded 5-sulfamoyl-1,2-benzisoxazole-3-acetamide (**24**) as a sole product.

4) H.R. Snyder and N.E. Boyer, *J. Am. Chem. Soc.*, **77**, 4233 (1955).



Formylation of 1

With ethyl formate and sodium hydride in acetic acid, **1** afforded 1,2-benzisoxazole-3-acetaldehyde (**25**). The IR spectrum of **25** revealed absorption bands due to a hydroxyl group at 3500—2900 cm^{-1} and a carbonyl group at 1725 cm^{-1} . The structure of **25** was determined by the formation of its oxime (**26**), mp 114—116°.

It could be noticed that the site of the electrophilic substitution of **1** altered depending on species of electrophiles and reaction conditions. Thus, in the halogenation of **1**, α -methylene group was the only position which was attacked by halogen and the nucleus was not substituted. In the chlorosulfonation of **1**, α -methylene group was substituted at first to give **17** and then 5-position of the nucleus was substituted to give **18**. On the other hand, the nitration occurred to 5-position of the nucleus at first to give **6**. Then α -methylene group of the 5-nitro derivative was substituted by nitro groups.

As mentioned in the previous paper,³⁾ it is of interest that α -methylene group of **1**, free acid, seems to be more active than that of **13** and **15**. That is, for instance, in the nitration of **13** and **15**, only the 5-position was nitrated and α -methylene group of **13** and **15** was left intact.

One of the feasible explanation for the unusual activation of α -methylene group of **1** would be as follows: the carboxyl group of **1** forms a hydrogen bond with the nitrogen at 2-position of the nucleus and the nitrogen attracts electron to activate α -methylene group (A). Or it may be also possible that **1** may form an intermediate complex with an electrophile which may attack α -methylene group intramolecularly (B).

Experimental⁵⁾

Chlorination of 1,2-Benzisoxazole-3-acetic Acid (1)—a) With Chlorine: In a solution of Cl_2 (2.8 g, 0.04 mol) in AcOH (40 ml) was dissolved **1** (6.3 g, 0.036 mol). The mixture was stirred for 3 hr at room temperature and then poured into H_2O . The oily substance was extracted with benzene and the benzene solution was washed with H_2O , dried over Na_2SO_4 and evaporated *in vacuo*. The residue was recrystallized from benzene to give α -chloro-1,2-benzisoxazole-3-acetic acid (**2**) (3.7 g, 48.6%), mp 133–135° (dec.). *Anal.* Calcd. for $\text{C}_8\text{H}_6\text{ClNO}_3$: C, 51.08; H, 2.86; Cl, 16.76; N, 6.63. Found: C, 51.21; H, 2.62; Cl, 16.90; N, 6.57.

The mother liquor of the recrystallization of **2** was evaporated and the residue was chromatographed on silica gel. With benzene, 3-dichloromethyl-1,2-benzisoxazole (**3**) (0.36 g, 5.0%) was eluted. *Anal.* Calcd. for $\text{C}_8\text{H}_5\text{Cl}_2\text{NO}$: C, 47.55; H, 2.49; Cl, 35.10; N, 6.93. Found: C, 47.14; H, 2.57; Cl, 34.70; N, 6.76. NMR (CDCl_3) δ : 7.14 (1H, s, CHCl_2). MS *m/e*: 201 (M^+), (205, 203).

b) With NCS (1.1 Molar Equivalent): To a solution of **1** (1.77 g, 0.01 mol) in CCl_4 (20 ml) was added NCS (1.5 g, 0.011 mol). The mixture was refluxed for 1 hr and CHCl_3 (50 ml) was added to the mixture. The mixture was extracted with 1 N NaOH soln. The organic layer was washed with H_2O , dried over Na_2SO_4 and evaporated *in vacuo* to give 0.5 g (24%) of crude **3**.

The alkaline extracts was neutralized with HCl and then extracted with benzene. The benzene solution was washed with H_2O , dried over Na_2SO_4 and evaporated. The residue was recrystallized from benzene to give 0.6 g (30%) of **2**.

c) With NCS (4 Molar Equivalent): To a solution of **1** (1.77 g, 0.01 mol) in CCl_4 (20 ml) was added NCS (5.35 g, 0.04 mol). The mixture was refluxed for 7 hr, filtered, washed with H_2O and dried over Na_2SO_4 . The solvent was removed *in vacuo* and the residual oil was chromatographed on silica gel. A mixture (1.6 g) of **3** and 3-trichloromethyl-1,2-benzisoxazole (**4**) was eluted with benzene.

d) With Iodine Monochloride (ICl): To a solution of **1** (1.77 g, 0.01 mol) in CCl_4 (20 ml) was added ICl (6.5 g, 0.04 mol). The mixture was refluxed for 2 hr and poured into H_2O . The product was extracted with CHCl_3 . The extracts was washed with H_2O , dried over Na_2SO_4 and evaporated. The residual oil was chromatographed on silica gel. With hexane, **4** (0.7 g, 30.0%) was eluted. *Anal.* Calcd. for $\text{C}_8\text{H}_4\text{Cl}_3\text{NO}$: C, 40.63; H, 1.70; Cl, 44.98; N, 5.92. Found: C, 40.46; H, 1.59; Cl, 44.58; N, 5.96. MS *m/e*: 235 (M^+), (235, 237, 239).

Iodination of 1 with ICl —To a solution of **1** (6.3 g, 0.03 mol) in AcOH (40 ml) was added ICl (6.4 g, 0.039 mol). The mixture was stirred for 5 hr at room temperature and then poured into H_2O . The product was extracted with benzene and the benzene solution was washed with H_2O , dried over Na_2SO_4 and evaporated. The residual oil was crystallized from benzene to give α -iodo-1,2-benzisoxazole-3-acetic acid (**5**) (1.5 g, 14%), mp 140–142° (dec.). *Anal.* Calcd. for $\text{C}_8\text{H}_6\text{INO}_3$: C, 35.67; H, 2.00; I, 41.88; N, 4.62. Found: C, 35.72; H, 1.88; I, 40.73; N, 4.63.

Nitration of 1—a) A mixture of **1** (5.0 g) and HNO_3 ($d=1.5$, 50 ml) was stirred under cooling in an ice-bath for 30 min. The mixture was poured into ice- H_2O and the precipitate was collected, washed with H_2O and dried. The crude product was added to EtOH . The insoluble material in EtOH was crystallized from benzene to give bis(5-nitro-1,2-benzisoxazol-3-yl)furoxan (**8**) (0.5 g, 9%), mp 206–209°. *Anal.* Calcd. for $\text{C}_{16}\text{H}_6\text{N}_6\text{O}_8$: C, 46.84; H, 1.47; N, 20.48. Found: C, 47.13; H, 1.43; N, 20.47. NMR ($\text{DMSO}-d_6$) δ : 8.20 (2H, d, $J=10$ Hz), 8.67 (1H, d.d, $J=2$ and 10 Hz), 8.68 (1H, d.d, $J=2$ and 10 Hz), 8.98 (1H, d, $J=2$ Hz), 9.12 (1H, d, $J=2$ Hz).

The ethanolic solution was evaporated *in vacuo* and the residue was recrystallized from EtOH to give 3-dinitromethyl-5-nitro-1,2-benzisoxazole (**7**) (1.5 g, 20%), mp 117–122°. *Anal.* Calcd. for $\text{C}_8\text{H}_4\text{N}_4\text{O}_7$: C, 35.83; H, 1.50; N, 20.89. Found: C, 36.41; H, 1.36; N, 20.91.

The aqueous filtrate was evaporated *in vacuo* and the residue was dissolved in benzene. The insoluble material was collected and recrystallized from AcOEt to give 5-nitro-1,2-benzisoxazole-3-acetic acid (**6**) (1.5 g, 24%), mp 210–212° (dec.). *Anal.* Calcd. for $\text{C}_8\text{H}_6\text{N}_2\text{O}_5$: C, 48.65; H, 2.72; N, 12.61. Found: C, 48.84; H, 2.54; N, 12.62.

b) To 50 ml of HNO_3 ($d=1.5$) was added **1** (5.0 g) under cooling in an ice-bath. The mixture was stirred for 1 hr under cooling and at room temperature for 2 hr. The mixture was poured into ice- H_2O and resulting precipitate was collected. The dried precipitate was added to benzene and the mixture was stirred for 30 min and insoluble material was collected. The crystallization of insoluble material from benzene gave 5-nitro-1,2-benzisoxazole-3-carboxylic acid (**12**) (1.5 g, 24%), mp 149–152°. *Anal.* Calcd. for $\text{C}_8\text{H}_4\text{N}_2\text{O}_5 \cdot 2/3\text{H}_2\text{O}$: C, 43.64; H, 2.13; N, 12.73. Found: C, 43.22; H, 2.21; N, 12.91. NMR ($\text{DMSO}-d_6$) δ : 7.17 (1H, d, $J=10$ Hz), 8.35 (1H, d.d, $J=10$ and 3 Hz), 8.57 (1H, d, $J=3$ Hz).

The benzene filtrate was evaporated *in vacuo* and the residue was washed with benzene to give 1.6 g (21%) of **7**.

5) All melting points are uncorrected. NMR spectra were taken with a Varian A-60 spectrometer using TMS as an internal standard; s, singlet; d, doublet; d.d, double doublet; MS spectra with a Hitachi RMU-6L mass spectrometer, and IR spectra with a 215 Hitachi Grating Infrared spectrophotometer.

The aqueous filtrate was evaporated *in vacuo* and the oily residue was chromatographed on silica gel. The fraction eluted with benzene-hexane (1:1) was evaporated to give 5-nitro-3-trinitromethyl-1,2-benzisoxazole (10) (0.3 g, 3%), mp 122–124° (dec.). *Anal.* Calcd. for $C_8H_3N_5O_9$: C, 30.68; H, 0.96; N, 22.37. Found: C, 31.08; H, 0.81; N, 21.50. NMR (CD_3COCD_3) δ : 8.33 (1H, d, $J=9$ Hz), 8.88 (1H, d.d, $J=9$ and 2 Hz), 9.25 (1H, d, $J=2$ Hz). MS m/e : 313 (M^+).

The fraction eluted with benzene was evaporated and 0.6 g of a mixture of 8 and 5-nitrobenzisoxazole-3-carboxaldehyde (11) was obtained. The mixture was dissolved in MeOH and 0.1 g of 8 was obtained as insoluble material. The methanolic solution was evaporated *in vacuo* and the residual oil was crystallized from ether-hexane to give 0.2 g (4%) of 11, mp 106–108°. *Anal.* Calcd. for $C_8H_4N_2O_4$: C, 50.01; H, 2.00; N, 14.58. Found: C, 50.29; H, 1.84; N, 14.75. NMR ($CDCl_3$) δ : 10.47 (1H, s, CHO), 7.85 (1H, d, $J=9$ Hz), 8.60 (1H, d.d, $J=2$ and 9 Hz), 9.01 (1H, d, $J=2$ Hz).

Nitration of Methyl 1,2-Benzisoxazole-3-acetate (13)—To cooled HNO_3 ($d=1.5$, 50 ml) was added 13 (5.0 g) and the mixture was stirred for 1 hr under cooling in an ice-bath. The mixture was poured into ice- H_2O and the separated oil was extracted with benzene. The benzene extracts was washed with H_2O , dried over Na_2SO_4 and evaporated. The residual oil was chromatographed on silica gel. The fraction eluted with benzene was evaporated and the residue was crystallized from MeOH to give 14, mp 66–67°. *Anal.* Calcd. for $C_{10}H_8N_2O_5$: C, 50.85; H, 3.41; N, 11.86. Found: C, 50.79; H, 3.13; N, 11.95. NMR ($DMSO-d_6$) δ : 3.72 (3H, s, CH_3), 4.40 (2H, s, CH_2), 7.99 (1H, d, $J=9$ Hz), 8.53 (1H, d.d, $J=2$ and 9 Hz), 8.97 (1H, d, $J=2$ Hz).

Nitration of 1,2-Benzisoxazole-3-acetonitrile (15)—To 15 (5.0 g) was added cooled HNO_3 ($d=1.5$, 50 ml) and the mixture was stirred for 1 hr under cooling in an ice-bath. The mixture was poured into ice- H_2O . The precipitate was collected and recrystallized from MeOH to give 5-nitro-1,2-benzisoxazole-3-acetonitrile (16) (5.8 g, 90%), mp 124–126°. *Anal.* Calcd. for $C_9H_5N_3O_3$: C, 53.21; H, 2.48; N, 20.68. Found: C, 53.45; H, 2.34; N, 20.94. NMR ($CDCl_3$) δ : 4.75 (2H, s, CH_2), 8.03 (1H, d, $J=9$ Hz), 8.55 (1H, d.d, $J=2$ and 10 Hz), 8.98 (1H, d, $J=2$ Hz).

Chlorosulfonation of 1—To $ClSO_3H$ (20 ml) was added 1 (3.5 g) and the mixture was heated at 60° for 7 hr. After being cooled, the mixture was poured into ice- H_2O . To the oily substance separated by decantation, was added cold NH_4OH (28%, 30 ml). After being stirred for 1 hr at room temperature, the mixture was concentrated *in vacuo*. The residue was dissolved in $AcOEt$ (300 ml) and insoluble material was filtered off. The filtrate was concentrated and the residue was submitted to the column chromatography on silica gel. The fraction eluted with $CHCl_3$ -MeOH (9:1) was evaporated and 3-sulfamoylmethyl-1,2-benzisoxazole (17) (0.7 g, 17%), mp 160–163°, was obtained. *Anal.* Calcd. for $C_8H_8N_2O_3S$: C, 45.27; H, 3.80; N, 13.20; S, 15.11. Found: C, 44.95; H, 3.60; N, 13.55; S, 15.01.

From the fraction eluted with $CHCl_3$ -MeOH (7:3), 3-sulfamoylmethyl-5-sulfamoyl-1,2-benzisoxazole (18) (0.2 g, 4%), mp 227–230° was obtained. *Anal.* Calcd. for $C_8H_8N_3O_5S_2$: C, 32.98; H, 3.11; N, 14.42; S, 22.02. Found: C, 33.04; H, 3.08; N, 14.66; S, 21.73.

Chlorosulfonation of 1,2-Benzisoxazole-3-acetonitrile (15)—A mixture of $ClSO_3H$ (40 ml) and 15 (6.4 g) was heated at 60° for 4 hr. The mixture was poured into ice- H_2O . The precipitate was collected and added to cold NH_4OH (28%, 30 ml). The mixture was stirred at room temperature for 1 hr and the resulting precipitate was collected, washed with H_2O and dried. The recrystallization from MeOH gave 4.5 g (46.5%) of 5-sulfamoyl-1,2-benzisoxazole-3-acetamide (24), mp 222–225°. *Anal.* Calcd. for $C_9H_9N_3O_4S$: C, 42.35; H, 3.55; N, 16.46; S, 12.56. Found: C, 42.29; H, 3.44; N, 16.55; S, 12.38.

Oxime of 1,2-Benzisoxazole-3-acetaldehyde (25)—To a solution of 1 (17.7 g) and $HCOOEt$ (120 ml) in benzene (500 ml) was added NaH (50%, 14.0 g) under cooling. The mixture was stirred for 3 hr in an ice-bath and allowed to stand at room temperature overnight. To the benzene solution was added H_2O (2 l) and the mixture was stirred for 40 min. The organic layer was separated and the solvent was removed *in vacuo*. Thus, crude 25 was obtained as an oily residue. The crude 25 was dissolved in benzene and an ethanolic solution of NH_2OH (prepared from $NH_2OH \cdot HCl$ 11.8 g, Na 4.2 g and $EtOH$ 200 ml) was added to the solution. The mixture was kept at room temperature for 30 min. The solvent was removed *in vacuo*. The residue was dissolved in benzene and insoluble material was collected. The solid was dissolved in hot H_2O (200 ml) and cooled. The precipitate was collected, washed and dried. The recrystallization from ether and hexane gave 7 g of the oxime (26), mp 114–116°. *Anal.* Calcd. for $C_9H_8N_2O_2$: C, 61.36; H, 4.58; N, 15.90. Found: C, 16.19; H, 4.46; N, 15.58.

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