

The Reactions of Sodium 1-Benzyl-1,4-dihydronicotinamide-4-sulfinate with Halogen Compounds

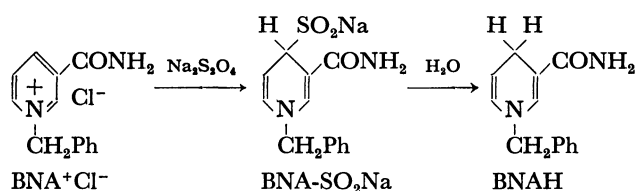
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Sodium 1-benzyl-1,4-dihydronicotinamide-4-sulfinate (BNA-SO₂Na) reacts with various halogen compounds, YZCHBr, through the cleavage of the carbon-sulfur bond to give sulfones, (YZCH)₂SO₂, in Y=Ph or PhCH=CH and Z=H; *trans*-stilbene in Y=Ph and Z=CH(Br)Ph or CH(OCH₃)Ph; and the reduction products, YZCH₂ and (YZCH)₂, in Y=Ph, Z=Br, and Y=H, Z=PhCO. The BNA-SO₂Na is converted to 1-benzyl-1,4-dihydronicotinamide (BNAH), while sulfur dioxide or sulfite ions are formed.

Sodium 1-benzyl-1,4-dihydronicotinamide-4-sulfinate (BNA-SO₂Na) is a bright-yellow intermediate isolated in the course of the reduction of 1-benzyl-1,4-dihydronicotinamide chloride (BNA⁺Cl⁻) with sodium dithionite to 1-benzyl-1,4-dihydronicotinamide (BNAH).¹⁾ The BNA-SO₂Na was characterized by NMR spectroscopy as an addition compound with the sulfinate group at the 4-position of BNAH.²⁾



The reaction of BNA-SO₂Na with organic compounds has not yet been reported except for the reduction of pyridinium salts to dihydropyridines.¹⁾ On the other hand, the reducing agents with a sulfinate group, such as sodium dithionite,³⁾ sodium hydroxymethanesulfinate,⁴⁾ and thiourea dioxide,⁵⁾ are well known. In view of the reducing action of these agents and BNAH, BNA-SO₂Na might also serve as a reducing agent with the cleavage of the carbon-sulfur bond of BNA-SO₂Na. Our interest in the reactivity of BNA-SO₂Na has led us to examine the reactions of BNA-SO₂Na with organic halogen compounds, of which the carbon-halogen bond reductions with metals⁶⁾ and metal complexes⁷⁾ and by electrolysis⁸⁾ have been studied extensively. In this paper, we wish to report on the reactions of BNA-SO₂Na with halogen compounds which have a phenyl, cinnamyl, or carbonyl group at the same carbon position as that of the halogen atom.

Results and Discussion

Formation of Sulfones. As Table 1 shows, the reaction of BNA-SO₂Na with benzyl bromide (**1**) in methanol or *N,N*-dimethylformamide (DMF) at 60 °C afforded dibenzyl sulfone, together with BNA⁺Br⁻. This reaction did not occur at 25 °C. The reduction products, such as toluene and 1,2-diphenylethane, were not obtained at all. Thus, the carbon-sulfur bond of BNA-SO₂Na was cleaved by the action of **1** to form BNA⁺Br⁻. The production of dibenzyl sulfone with BNA⁺Br⁻ in equimolar amounts indicates that the Na⁺ or BNA⁺ salt of phenylmethanesulfinic acid (**2**) is formed as an intermediate, and that it then reacts with **1** to give dibenzyl sulfone:



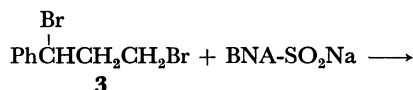
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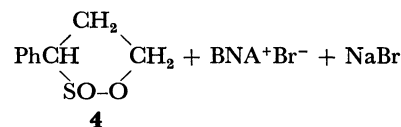
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A substitution by the sulfinate group was found to take place in the reaction of BNA-SO₂Na with 1,3-dibromo-1-phenylpropane (**3**). As Table 1 shows, a cyclic sulfinate (**4**) was produced by ring-closure in amounts corresponding approximately to those of BNA⁺Br⁻:



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Cinnamyl bromide (**5**) also reacted with BNA-SO₂Na in 80 vol% aqueous acetone or DMF, even at 25 °C, to give dicinnamyl sulfone in a high yield, together with BNA⁺Br⁻, as Table 1 shows.

TABLE 1. REACTIONS OF BNA-SO₂Na WITH **1**, **3**, AND **5**^{a)}

Halogen compd	Reaction conditions	-SO ₂ - or -SO-O- % ^{b)}	BNA ⁺ Br ⁻ % ^{b)}
1	MeOH, 60 °C, 6 h	67	62
1	DMF, 60 °C, 3 h	69	— ^{c)}
3	EtOH, 60 °C, 3 h	55	64
3	DMF, 60 °C, 3 h	64	71
5	(CH ₃) ₂ CO-H ₂ O (4:1) 25 °C, 3 h	83	86
5	DMF, 25 °C, 3 h	99	96

a) BNA-SO₂Na; **5**—5.1 mmol. Solvent; 50 cm³. BNA-SO₂Na/halogen compd molar ratio; 1. b) Based on the halogen compound (2×product or BNA⁺Br⁻ (mol)/halogen compd (mol)×100). The products obtained from **1**, **3**, and **5** are dibenzyl sulfone, **4**, and dicinnamyl sulfone respectively. c) Identified, but not quantified.

Formation of Olefins. When a solution of *dl* or *meso*-1,2-dibromo-1,2-diphenylethane (*dl* or *meso*-**6**) in ethanol containing BNA-SO₂Na was heated at 60 °C, the *dl* and *meso*-**6** were converted to *trans*-stilbene in high yields, as Table 2 shows. On the other hand, *cis*-stilbene was not obtained at all. The BNA-SO₂Na was converted to BNA⁺Br⁻ with the generation of sulfur dioxide. The addition of water to the reaction system

(80 vol% aqueous ethanol) did not affect the yield of *trans*-stilbene. When DMF was used as the solvent, the reaction occurred rapidly, even at 20 °C. Furthermore, the isomerization of *cis*-stilbene to *trans*-stilbene was not observed under the reaction conditions.

threo-1-Bromo-2-methoxy-1,2-diphenylethane (*threo*-**7**) reacted also with BNA-SO₂Na in ethanol and DMF at 60 °C to give, selectively, *trans*-stilbene, although the reaction took place slowly (Table 2). Thus, BNA-SO₂Na underwent the debromination of the *dl* and *meso*-**6** and *threo*-**7**, resulting selectively, in *trans*-stilbene, with BNA⁺Br⁻ and sulfur dioxide also formed.

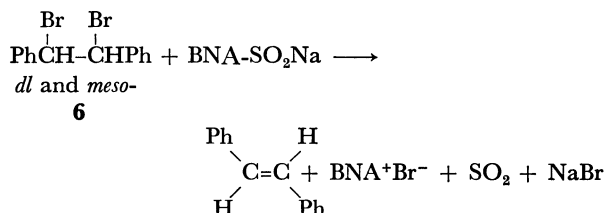
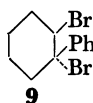
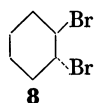


TABLE 2. REACTIONS OF BNA-SO₂Na WITH *dl* AND *meso*-**6** AND *threo*-**7**^{a)}

6 or 7	Molar ratio ^{b)}	Solvent	Product, %		
			PhCH=CHPh	BNA ⁺ Br ⁻	SO ₂
<i>dl</i> ^{c)}	1	EtOH	73 ^{e)}	80	57
<i>dl</i>	1	DMF	76	78	— ^{f)}
<i>meso</i>	2	EtOH	94	— ^{f)}	50
<i>meso</i>	2	DMF	99	— ^{f)}	— ^{f)}
<i>threo</i> ^{d)}	2	EtOH	48 ^{g)}	—	—
<i>threo</i>	1	DMF	39 ^{g)}	—	—

a) **6** or **7**; 3 mmol. Solvent; 50 cm³. Reaction time; 2 h. Temperature; 60 °C. The yields were calculated by means of product (mol)/**6** or **7** (mol) × 100. b) BNA-SO₂Na/**6** or **7**. c) In the case of the molar ratio of 2, *trans*-stilbene was obtained in a 100% yield. d) Reaction time; 3 h. e) Recovery % of *dl*-**6**; 27%. f) Identified, but not quantified. g) Recovery % of *threo*-**7**; 40% (EtOH) and 55% (DMF).

In order to investigate whether or not the existence of the phenyl group in *vic*-dibromides is required for debromination, the reactions of BNA-SO₂Na with *trans*-1,2-dibromocyclohexane (**8**) and *trans*-1-phenyl-1,2-dibromocyclohexane (**9**) in ethanol at 60 °C were carried out. The **8** was recovered unchanged after a reaction of 6 h, but the **9** was converted to 1-phenylcyclohexene in a 77% yield after 2 h. BNA⁺Br⁻ was obtained in a 86% yield, together with 90% of the sulfur dioxide. Thus, the phenyl group attached to the carbon atom with the bromine atom favors the debromination of *vic*-dibromides by BNA-SO₂Na.



The debromination of *dl* and *meso*-**6** by many dehalogenating agents has been studied extensively.⁹⁾ Among these reagents, the benzenesulfinate ion has been known to undergo the debromination of *dl*-**6** to give *cis*-stilbene as the major product.⁹⁾ Thus, the reactivity of BNA-

SO₂Na to *dl*-**6** would differ essentially from that of the benzenesulfinate ion.

Reduction. Benzyldiene dibromide (**10**) was converted to *dl*-**6** and *trans*-stilbene by the action of BNA-SO₂Na in water-free DMF at 20 °C, as Table 3 shows. This reaction was accompanied by the conversion of BNA-SO₂Na to BNA⁺Br⁻ and sulfur dioxide. When the molar ratio of BNA-SO₂Na to **10** was 2, *trans*-stilbene was obtained as the only product. The *trans*-stilbene must be produced by the debromination of *dl*-**6** by BNA-SO₂Na, as has been described above. In 80 vol% aqueous methanol, however, dibenzyl sulfone was obtained without any formation of *dl*-**6** or *trans*-stilbene. Thus, it is possible that the formation of **1** is the intervening process in the conversion of **10** to dibenzyl sulfone and that, in the process, BNA-SO₂Na undergoes the two-electron reduction of **10** to give **1**. In an aprotic solvent, the Ph $\dot{\text{C}}\text{HBr}$ produced by the two-electron reduction could react with **10** to give *dl*-**6**.

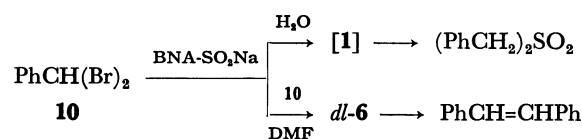


TABLE 3. REACTION OF BNA-SO₂Na WITH **10**^{a)}

Reaction conditions ^{b)}	Product, % ^{c)}
DMF, 20 °C, 3 h (1)	<i>dl</i> - 6 (26); PhCH=CHPh (36)
DMF, 20 °C, 3 h (2)	PhCH=CHPh (69)
MeOH-H ₂ O (80%), 60 °C, 3 h (2)	(PhCH ₂) ₂ SO ₂ (36)

a) **10**; 5–6 mmol. Solvent; 50 cm³. b) The parentheses represent the molar ratio of BNA-SO₂Na to **10**. c) Based on **10** (2 × product (mol)/**10** (mol) × 100. BNA⁺Br⁻ and sulfur dioxide were identified, but not quantified.

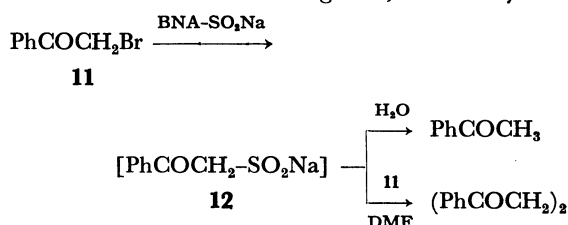
α-Bromoacetophenone (**11**) was reduced with BNA-SO₂Na in 80 vol% aqueous methanol at 30 °C to give acetophenone in a good yield, as Table 4 shows. In the reaction, BNA⁺Br⁻ and a sulfite ion were produced from BNA-SO₂Na in amounts corresponding to those of acetophenone. No further reduction of acetophenone with BNA-SO₂Na occurred at all. As BNA-SO₂Na is known to be converted to BNAH and a sulfite ion by the action of water, there is a possibility that BNAH acts as a reducing agent. Therefore, the reduction of **11** with BNAH was carried out under similar conditions. Consequently, it was found that the rate of the reduction by BNAH is much slower than that by BNA-SO₂Na: the reduction of **11** with BNAH in 80 vol% aqueous methanol at 25 °C gave acetophenone in a 16% yield after a reaction of 24 h. Furthermore, the reaction of **11** with BNA-SO₂Na was carried out using water-free DMF as the solvent. As Table 4 shows, 1,2-dibenzoylthane was obtained as the reduction product in a high yield, without any formation of 2,4-diphenylfuran, which is produced in the dehalogenation of **11** with Cr(II) or Cu(I) salt¹⁰⁾ in DMF or DMSO. BNA-SO₂Na was converted to BNA⁺Br⁻ with the generation of sulfur dioxide. The selective formation of acetophenone or 1,2-dibenzoylthane suggests that the reaction of **11** with BNA-SO₂Na proceeds *via* the formation of **12**, which reacts as a carbanion, PhCO-

TABLE 4. REACTIONS OF BNA-SO₂Na WITH α -BROMO CARBONYL COMPOUNDS^{a)}

YZCHBr Y Z		Reaction conditions ^{b)}	Reduction product, %	BNA+Br ⁻ %	SO ₃ ²⁻ , SO ₂ %
H	PhCO	M-W, 30 °C, 6 h	PhCOCH ₃ (67)	67	61
H	PhCO	DMF, 30 °C, 3 h	(PhCOCH ₂) ₂ (80)	86	— ^{c)}
Ph	PhCO	M-W, 20 °C, 3 h	PhCOCH ₂ Ph (82)	89	— ^{c)}
Ph	EtOCO	M-W, 25 °C, 6 h	PhCH ₂ CO ₂ Et (82)	88	84
EtOCO	EtOCO	M-W, 20 °C, 6 h	CH ₂ (COOEt) ₂ (81)	79	75

a) YZCHBr; 3—5 mmol. Solvent; 50 cm³. BNA-SO₂Na/YZCHBr molar ratio=1. b)M-W represents 80 vol% MeOH-H₂O. c) Identified, but not quantified.

CH₂⁻, followed by a reaction with water to give acetophenone or with **11** in DMF to give 1,2-dibenzoylthane.



α -Bromodeoxybenzoin, ethyl α -bromophenylacetate, and diethyl α -bromomalonate were all reduced with BNA-SO₂Na in 80 vol% aqueous methanol at 20 °C to the corresponding parent carbonyl compounds in high yields. These reactions were accompanied by the formation of equimolar amounts of BNA+Br⁻ and a sulfite ion. Thus, the carbonyl group attached to the carbon atom with a bromine atom favors the reductive debromination by BNA-SO₂Na.

Experimental

Materials. All the halogen compounds, except for **1**, were prepared according to the methods described in the literature.¹¹⁾ The BNA-SO₂Na was prepared from BNA+Cl⁻ and sodium dithionite (85—90% purity) according to the method reported by Biellmann and Callot,¹⁾ and was purified in the following manner: BNA-SO₂Na was dissolved in a 1 M sodium hydroxide solution at 40 °C, and the solution was allowed to cool to 0 °C to give yellow crystals. After the mixture had then been filtered under nitrogen, the crystals were washed with cold water and dried under a reduced pressure of 1 Torr for 4—6 h. All the procedures were carried out in an atmosphere of nitrogen. The purified BNA-SO₂Na was immediately submitted to the reactions with halogen compounds. The UV and NMR spectra (1 M sodium hydroxide solution) of the BNA-SO₂Na used here were identical with those reported by Caughey and Schellenberg.²⁾

Reactions of BNA-SO₂Na. **Benzyl Bromide (1):** To a solution of 5.05 mmol of **1** in 50 cm³ of methanol, we added 5.13 mmol of BNA-SO₂Na. The suspension was stirred under nitrogen at 60 °C for 6 h. After the methanol had then been removed *in vacuo*, the residue was suspended in 150 cm³ of benzene, and heated under reflux, and the mixture was filtered. The benzene solution was concentrated to 10—15 cm³. The concentrate was submitted to chromatography on silica gel. Elution with benzene gave 0.42 g (67%) of dibenzyl sulfone; mp 149—150 °C (lit,¹²⁾ 149.5—150 °C). Its IR spectrum was identical with that of the authentic specimen. IR (KBr): 1110 and 1300 cm⁻¹ (SO₂). The precipitate was then added to 50 cm³ of methanol, and heated under reflux,

and the mixture was filtered. After methanol removal *in vacuo*, the residue was again added to 50 cm³ of acetone containing a small amount of ethanol and refluxed. The insoluble material was separated from the solution by filtration. The removal of the solvent *in vacuo* gave 0.45 g (62%) of BNA+Br⁻; mp 207—209 °C. Its melting point and IR spectrum were identical with those of the authentic specimen prepared from **1** and nicotinamide. Similar procedures were used in the experiment employing DMF as a solvent.

1,3-Dibromo-1-phenylpropane (3): The reaction of BNA-SO₂Na (5.05 mmol) with **3** (5.11 mmol) was carried out, employing ethanol (50 cm³) as the solvent, under conditions similar to those used in the case of **1**. The reaction products were isolated in a manner similar to that described above to yield 0.5 g (55%) of **4** and 0.93 g (64%) of BNA+Br⁻. The **4** exhibited NMR (CCl₄) signals at δ =2.6 (m, 2H, CH₂), 4.3 (m, 2H, CH₂O), 4.9 (m, 1H, CH), and 7.3 ppm (s, 5H, aromatic protons), and an IR (KBr) peak at 1120 cm⁻¹ (SO₂). MS, *m/e*, 182 (parent peak).

Found: C, 59.02; H, 5.66%. Calcd for C₉H₁₀SO₂: C 59.33; H, 5.53%.

Cinnamyl Bromide (5): A solution of 5.03 mmol of **5** and 5.09 mmol of BNA-SO₂Na in 50 cm³ of DMF was stirred under nitrogen at 25 °C for 3 h. The reaction mixture was then poured into 300 cm³ of water to give 0.74 g (99%) of dicinnamyl sulfone; mp 199—200 °C: NMR (CCl₄) δ =3.72 (d, CH₂SO₂) (total 4H), 6.40 (m, =CH) (total 2H), and 7.14 ppm (s, C₆H₅CH=) (total 12H); IR (KBr) 970 (HC=CH) and 1050 and 1180 cm⁻¹ (SO₂); MS, *m/e*; 64 (SO₂), 117 (C₆H₅-CH=CHCH₂), and 234 [(C₆H₅CH=CHCH₂)₂].

Found: C, 72.53; H, 6.17%. Calcd for C₁₈H₁₈SO₂: C, 72.46; H, 6.08%.

After the water and DMF had been removed *in vacuo*, the residue was extracted with methanol to yield 0.71 g (96%) of BNA+Br⁻ in a manner similar to that described above.

vic-Dibromides (dl and meso-6, 8, and 9) and threo-7: A typical experiment was as follows: to a solution of 3 mmol of *dl*-**6** in 50 cm³ of ethanol, we added 3.04 mmol of BNA-SO₂Na. The mixture was stirred at 60 °C for 2 h while nitrogen was being bubbled through the solution. The sulfur dioxide thus evolved was absorbed by 50 cm³ of a 1 M sodium hydroxide solution. To the alkaline solution we added 20 cm³ of a 30% hydrogen peroxide solution, and then an excess of a barium chloride solution. The precipitate of barium sulfate was obtained by filtration. Yield: 0.4 g (57%). After the ethanol had been removed *in vacuo*, the residue was extracted with ether. The material, which was insoluble in ether, was then added to methanol. BNA+Br⁻ was isolated from the methanol solution by procedures similar to those used in the case of **1**. Yield: 0.71 g (80%). The crude product obtained by the evaporation of the ethereal phase was chromatographed on silica gel to yield *trans*-stilbene (0.394 g, 73%) (mp 118—120 °C), and *dl*-**6** (0.28 g, 27% recovery). Similar procedures were used for

the reactions of BNA-SO₂Na with *meso*-**6**, *threo*-**7**, **8**, and **9**.

Benzylidene Dibromide (10). DMF Solvent: To a solution of 6.06 mmol of **10** in 50 cm³ of DMF, we added 6.07 mmol of BNA-SO₂Na. The solution was stirred under nitrogen for 3 h at 20 °C, poured into 300 cm³ of water, and extracted with ether. After the removal of the water and DMF from the aqueous layer, BNA⁺Br⁻ was isolated in a 75% yield by procedures similar to those used in the case of **1**. The ethereal extract was dried on magnesium sulfate, and the ether was removed. The residue was submitted to chromatography on alumina. Elution with hexane and benzene gave 0.195 g (36%) of *trans*-stilbene and 0.26 g (26%) of *dl*-1,2-dibromo-1,2-diphenylethane respectively.

80 Vol% Aqueous Methanol: To a solution of 5.04 mmol of **10** in 50 cm³ of 80 vol% aqueous methanol, we added 10.1 mmol of BNA-SO₂Na. The solution was then stirred under nitrogen for 3 h at 60 °C. After methanol removal *in vacuo*, 50 cm³ of water was added to the concentrate. The resulting solution, containing the precipitate, was extracted with ether. The ethereal extract was dried over magnesium sulfate. The subsequent removal of the ether gave 0.22 g (36%) of dibenzyl sulfone.

α -Halo Ketones and Esters: A typical experiment was as follows: A solution of a mixture of 3.02 mmol of **11** and 3.01 mmol of BNA-SO₂Na in 50 cm³ of 80 vol% aqueous methanol was stirred under nitrogen at 30 °C for 6 h. Then water (200 cm³) was added, and the resulting solution was extracted with benzene. The benzene phase was dried over magnesium sulfate, and the benzene was then removed. The residue was chromatographed on silica gel to yield 0.244 g (67%) of acetophenone. The aqueous phase, containing a sulfite ion, was acidified by means of 30 vol% hydrobromic acid to bring about the evolution of sulfur dioxide. The sulfur dioxide thus evolved was absorbed by a 1 M sodium hydroxide solution and determined in a manner similar to that described above. Yield of sulfite ions: 61%. The crude product obtained by solvent evaporation was determined by the method described above to contain 0.59 g (67%) of BNA⁺Br⁻. Similar procedures were used for the reactions of BNA-SO₂Na with α -bromodeoxybenzoin, ethyl α -bromophenylacetate, and ethyl α -bromomalonate.

The reaction of BNA-SO₂Na (5.05 mmol) with **11** (5 mmol) in DMF (50 cm³) at 30 °C for 3 h yielded 0.48 g (80%) of 1,2-dibenzoylthane (mp 143–144 °C (lit.¹³) 145 °C), and 0.62 g (86%) of BNA⁺Br⁻. 1,2-Dibenzoylthane exhibited an IR (KBr) peak at 1675 cm⁻¹ (C=O). (Found: C, 80.88;

H, 5.88%. Calcd for C₁₆H₁₄O₂: C, 80.64; H, 5.92%).

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