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Reaction of Substituted Benzaldehydes with Sodium Hydrogensulfide or Sodium Sulfide in Liquid Ammonia

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Reactions of substituted benzaldehydes with sodium hydrogensulfide in the presence of nitrobenzene, nitrosobenzene, or azobenzene in liquid ammonia produce the corresponding benzyl alcohols and benzamides. On the other hand, reaction of benzaldehyde with sodium sulfide produces benzyl alcohol and benzamide. A reaction mechanism has been proposed which involves benzaldehyde anion radical.

The Cannizzaro reaction has been considered as one of the most fundamental reactions in organic chemistry.[1)] A variety of mechanisms for this reaction have been proposed,[2)] and the mechanism presently accepted involves a hydride transfer. Radical chain mechanisms have been suggested[3)] but discounted mainly because radical initiators or inhibitors have no significant effect on reaction rate.[4)] Recently, however, Chung[5)] has evidenced a possible involvement of radical intermediates in a Cannizzaro reaction consuming benzaldehyde-α-*d* in alkaline aqueous dioxane or dioxane alone; a formation of monodeuterated benzyl alcohol-α-d_1 suggests formation of benzaldehyde anion radical, followed by hydrogen atom abstraction from solvent. Ashby *et al.*[6)] have studied reaction of benzaldehydes having electron-withdrawing substituents with NaOH in THF/HMPA (9:1) by EPR spectroscopy and obtained evidence for existence of paramagnetic species in solution. In our previous paper,[7)] we have reported that reaction of 9-nitroanthracene with NaSH in liquid ammonia gave 10,10′-di-aci-nitro-9,9′,10,10′-tetrahydro-9,9′-bianthryl, di-9-anthryl disulfide, anthracene, and anthraquinone. These products suggest formation of 9-nitroanthracene anion radical by transfer of electron generated from NaSH–liq NH_3 to 9-nitroanthracene. This result urged us to attempt oxidation-reduction reactions *via* single electron-transfer by using NaSH- or Na_2S–liq. NH_3. In this paper, we report results on reaction of substituted benzaldehydes with NaSH or Na_2S in liquid ammonia.

Results and Discussion

Benzaldehyde (**1**) reacts with liquid ammonia in the presence and absence of NaSH to give *N,N′*-dibenzylidene-α,α-toluenediamine quantitatively, and no such oxidation-reduction as the well-known Cannizzaro reaction occurs (Runs 1 and 2 in Table 1). However, addition of a small amount of nitrobenzene in this reaction system gave benzyl alcohol and benzamide in 27 and 25% yields, respectively, besides a small amount of *N*-benzylideneaniline (Run 3 in Table 1). On the other hand, reaction of **1** with $Na_2S\cdot5H_2O$ in liquid ammonia gave benzyl alcohol and benzamide in good yields without formation of *N,N′*-dibenzylidene-α,α-toluenediamine (Run 5 in Table 1). Reaction of substituted benzaldehydes with NaSH in the presence of nitrobenzene gave the corresponding benzyl alcohols and benzamides (Runs 6—9 in Table 1). This reaction was also catalyzed by nitrobenzene derivatives such as *m*-dinitrobenzene and 1,3,5-trinitrobenzene (Runs 2—4 in Table 2). On the other hand, no formation of benzyl alcohol or benzamide was effected by addition of either aromatic nitro compounds, such as *p*-dinitrobenzene, 1-nitronaphthalene,[8)] and 9-nitroanthracene,[7)] which give substitution products in reaction with NaSH in liquid ammonia, or nitro compounds, such as *p*-nitroaniline, *p*-nitrotoluene, and nitromethane, which have high polarographic half-wave potentials (Runs 5—10

Table 1. Reactions of substituted benzaldehydes with NaSH or $Na_2S\cdot5H_2O$ in liq·NH_3[a)]

$$R\text{—}C_6H_4CHO \xrightarrow[\text{liq}\cdot NH_3,\ 40\,°C,\ 5\,h]{NaSH\ \text{or}\ Na_2S\cdot5H_2O} R\text{—}C_6H_4CH_2OH + R\text{—}C_6H_4CONH_2$$

Run	Substituent R	Additive (mmol)	NaSH/mmol	$Na_2S\cdot5H_2O$/mmol	Yield/%	
					$R\text{—}C_6H_4CH_2OH$	$R\text{—}C_6H_4CONH_2$
1[b)]	H	—	—	—	0	0
2[b)]	H	—	2	—	0	0
3	H	Nitrobenzene (0.25)	2	—	27	25
4	H	Azobenzene (1)	2	—	35	32
5	H	—	—	2	37	37
6	2-OCH_3	Nitrobenzene (2)	2	—	43	34
7	4-OCH_3	Nitrobenzene (2)	2	—	32	—[c)]
8	4-CH_3	Nitrobenzene (2)	2	—	27	—[c)]
9	4-Cl	Nitrobenzene (2)	2	—	26	—[c)]

a) Substituted benzaldehyde: 2 mmol. Substituted *N*-benzylideneaniline were produced when nitrobenzene was added. b) *N,N′*-Dibenzylidene-α,α-toluenediamine was quantitatively obtained. c) Not determined.

TABLE 2. REACTIONS OF BENZALDEHYDE WITH NaSH IN THE PRESENCE OF A NITRO COMPOUND IN LIQ. NH_3[a]

Run	Nitro compound	(mmol)	Yield/% Benzyl alcohol
1	Nitrobenzene	(0.25)	27
2	*m*-Dinitrobenzene	(0.25)	24
3	*m*-Dinitrobenzene	(0.1)	34
4	1,3,5-Trinitrobenzene	(0.1)	28
5	1-Nitronaphthalene	(0.25)	4
6	*p*-Nitroaniline	(2.0)	Trace
7	*p*-Nitrotoluene	(2.0)	Trace
8	*p*-Dinitrobenzene	(2.0)	0
9	9-Nitroanthracene	(2.0)	0
10	Nitromethane	(2.0)	0

a) Benzaldehyde and NaSH: 2 mmol; liq·NH_3: 10 ml; temp: 40 °C; time: 5 h.

TABLE 3. REACTIONS OF BENZALDEHYDE WITH NaSH IN THE PRESENCE OF A REDUCTANT OF NITROBENZENE IN LIQ. NH_3[a]

Run	Reductant	NaSH/mmol	Yield/% Benzyl alcohol
1	PhNO	2	10
2	PhNHOH	2	0
3	PhN(O)=NPh	2	0
4	PhN=NPh	2	31
5	PhNHNHPh	2	0
6	$PhNH_2$	2	0
7	PhN=NPh	0	0
8	PhNHNHPh	0	0

a) Benzaldehyde and reductant: 2 mmol; liq·NH_3: 10 ml; temp: 40 °C; time: 5 h.

in Table 2). Because nitrobenzene was easily reduced by NaSH in liquid ammonia to give aniline, azobenzene, and other reductants,[8] we investigated whether the catalytic behavior for the formation of benzyl alcohol and benzamide was due to the addition of nitrobenzene or its reductant. Nitrobenzene, nitrosobenzene, and azobenzene were found to exhibit the catalytic behavior for the formation of benzyl alcohol as shown in Table 3. Azoxybenzene, phenylhydroxylamine, hydrazobenzene, and aniline did not exhibit the catalytic behavior. Moreover, reactions of nitrobenzene or its reductants with NaSH at 40 °C for 5 h in liquid ammonia were investigated, results obtained being shown in Table 4. Both nitrobenzene and nitrosobenzene, showing the catalytic behavior, reacted with NaSH in liquid ammonia to give azobenzene, whereas azobenzene, after allowed to react with NaSH, resulted in almost complete recovery of itself only with formation of a small amount of hydrazobenzene. Accordingly, azobenzene is one of catalyzers for the formation of benzyl alcohol and benzamide in the reaction of **1** with NaSH in liquid ammonia. However, we can't deny that nitrobenzene and nitrosobenzene themselves act also as catalyzers.

On the other hand, the reaction of **1** with $Na_2S\cdot5H_2O$ produced benzyl alcohol and benzamide in good yields (Run 5 in Table 1).

This reaction was investigated in such solvents as Et_2NH, Et_3N, MeOH, DMF, and HMPA, results obtained being shown in Table 5. The reaction with NaSH occurred only in such solvents[9,10] as liquid ammonia and HMPA which are favorable for single electron-transfer reaction,[11,12] but the reaction with $Na_2S\cdot5H_2O$ occurred in various organic solvents.

Attempted reaction of benzophenone with NaSH in the presence of azobenzene in liquid ammonia at 40 °C for 5 h resulted only in recovery of the substrate. An addition of formalin (37%) to this reaction system, however, led to formation of benzhydrol in 27% yield;

TABLE 4. REACTIONS OF NITROBENZENE OR ITS REDUCTANTS WITH NaSH IN LIQ. NH_3[a]

Run	Substrate	Yield/%						
		$PhNO_2$	PhNO	PhNHOH	PhN(O)=NPh	PhN=NPh	PhNHNHPh	$PhNH_2$
1	$PhNO_2$	62	0	0	0	Trace	0	26
2	PhNO	0	0	b)	0	37	b)	11
3	PhNHOH	0	0	b)	b)	0	b)	0
4	PhN(O)=NPh	0	0	0	0	0	99	0
5	PhN=NPh	0	0	0	0	92	8	0
6	PhNHNHPh	0	0	0	0	0	100	0
7	$PhNH_2$	0	0	0	0	0	0	100

a) Substrate and NaSH: 2 mmol; liq·NH_3: 10 ml; temp: 40 °C; time: 5h. b) Not determined.

TABLE 5. REACTIONS OF SUBSTITUTED BENZALDEHYDES WITH NaSH OR $Na_2S\cdot5H_2O$ IN VARIOUS SOLVENTS[a]

Run	Substituent R	Solvent	Additive (mmol)	NaSH/mmol	$Na_2S\cdot5H_2O$/mmol	Temp/°C	Yield/% Benzyl alcohol
1	H	Et_2NH	$PhNO_2$ (2)	2	—	Reflux	Trace
2	H	Et_3N	$PhNO_2$ (2)	2	—	Reflux	Trace
3	H	DMF	PhN=NPh (1)	2	—	80	Trace
4	H	HMPA	PhN=NPh (1)	2	—	80	20
5	4-Cl	Et_2NH	—	—	2	Reflux	7
6	4-Cl	Et_3N	—	—	2	Reflux	32
7	4-Cl	MeOH	—	—	2	Reflux	25
8	4-Cl	HMPA	—	—	2	80	35

a) Substituted benzaldehyde: 2 mmol; solvent: 4 ml; time: 5 h.

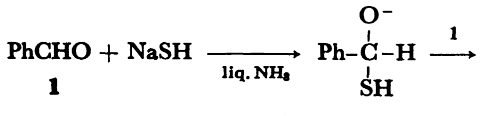
reaction with $Na_2S\cdot 5H_2O$ in the presence of formalin (37%) in liquid ammonia under the same conditions yielded benzhydrol in 58% yield. These results suggest that the methylenic hydrogen generated newly in the alcohol is not the hydrogen in H_2O, NH_3, or NaSH but the one in formaldehyde. Consequently, the formation of benzyl alcohol and benzamide in the reaction of substituted benzaldehydes with NaSH or $Na_2S\cdot 5H_2O$ in liquid ammonia is taken to be a result of an intermolecular reaction.

The following facts have been disclosed on the reaction of substituted benzaldehydes with NaSH in liquid ammonia.

1. The reaction with liquid ammonia in the absence and presence of NaSH produces *N,N′*-dibenzylidene-*α,α*-toluenediamine quantitatively.
2. The reaction proceeds only in the presence of an additive such as nitrobenzene, nitrosobenzene, or azobenzene which are good electron acceptors.
3. No sulfur-containing products are produced.
4. *N,N′*-dibenzylidene-*α,α*-toluenediamine formed by the reaction of benzaldehyde with ammonia does not react with NaSH in the presence of azobenzene in liquid ammonia.
5. The methylenic hydrogen generated newly comes from the formyl group in benzaldehydes.
6. The reaction proceeds only in liquid ammonia or HMPA.

Since **1** reacts with ammonia in the absence and presence of NaSH to give *N,N′*-dibenzylidene-*α,α*-toluenediamine quantitatively, the formation of benzyl alcohol and benzamide is not a simple Cannizzaro-like reaction *via* intermolecular reaction of **1** with hemiaminal, which has been formed from **1** and ammonia.

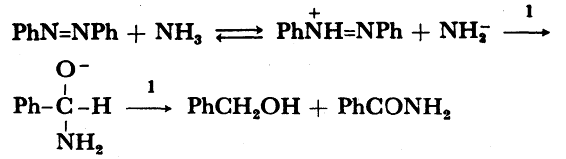
Another Cannizzaro-like reaction



$$\underset{\mathbf{1}}{\mathrm{PhCHO}} + \mathrm{NaSH} \xrightarrow[\text{liq. NH}_3]{} \mathrm{Ph{-}}\overset{\mathrm{O^-}}{\underset{\mathrm{SH}}{\mathrm{C}}}\mathrm{{-}H} \xrightarrow{\mathbf{1}}$$
$$\mathrm{PhCH_2OH + PhCOSH} \overset{\mathrm{NH_3}}{\nrightarrow} \mathrm{PhCONH_2 + H_2S}$$

is also conceivable. This mechanism, however, is also denied because in this reaction no sulfur-containing products are obtained and because the reaction of thiobenzoic acid with liquid ammonia at 40 °C for 5 h gives ammonium thiobenzoate quantitatively.

The other Cannizzaro-like reaction



$$\mathrm{PhN{=}NPh + NH_3} \rightleftharpoons \mathrm{Ph\overset{+}{N}H{=}NPh + NH_2^-} \xrightarrow{\mathbf{1}}$$
$$\mathrm{Ph{-}}\overset{\mathrm{O^-}}{\underset{\mathrm{NH_2}}{\mathrm{C}}}\mathrm{{-}H} \xrightarrow{\mathbf{1}} \mathrm{PhCH_2OH + PhCONH_2}$$

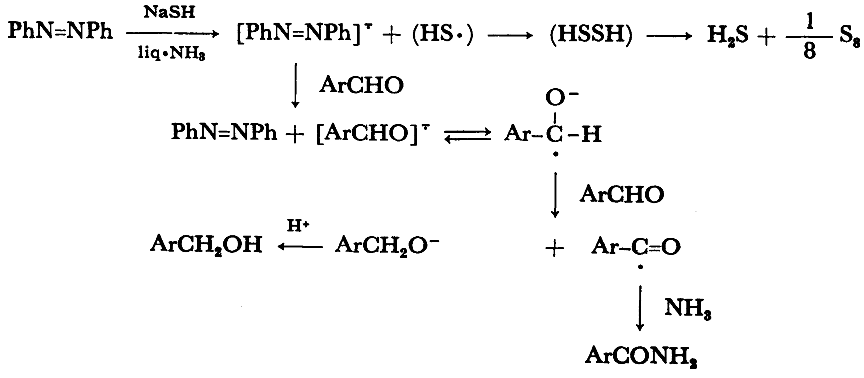
is also conceivable, but, in conflict with this sequence, the reaction of **1** with ammonia in the presence of azobenzene gives *N,N′*-dibenzylidene-*α,α*-toluenediamine, no benzyl alcohol or benzamide being formed (Run 8 in Table 3). Accordingly, this mechanism is also unlikely.

Meanwhile, as described above, the reduction of **1** by hydrazobenzene is also unlikely (Runs 5 and 8 in Table 3).

Since the reactions in question proceed only in the presence of an additive such as nitrobenzene, nitrosobenzene, or azobenzene which are good electron acceptors,[10,11] a reaction mechanism involving single electron-transfer, as shown in Scheme 1, may be considered as one of plausible mechanisms.

The polarographic half-wave potentials (−0.45—0.04 V in H_2O) of nitrobenzene, nitrosobenzene, and azobenzene are lower than those (−1.15—−0.77 V in H_2O) of substituted benzaldehydes and benzophenone. Accordingly, the initiation step is an electron–transfer to azobenzene from NaSH as an electron-donor species in liquid ammonia,[7] and the subsequent electron-transfer to benzaldehyde from azobenzene anion radical generates benzaldehyde anion radical. It then abstracts hydrogen atom from benzaldehyde to form benzyl alcoholate and benzoyl radical. The benzyl alcoholate in turn abstracts proton from solvent to afford benzyl alcohol. Meanwhile, the benzoyl radical reacts with NH_3 to afford benzamide. A solution of NaSH in HMPA at room temperature assumes an intense blue color. This solution liberate gradually H_2S and elemental sulfur according to

$$2\,\mathrm{NaSH} \xrightarrow{\text{HMPA}} (2\,\mathrm{Na^+\,e^-}) + (2\,\mathrm{HS\cdot}),$$
$$(2\,\mathrm{HS\cdot}) \longrightarrow (\mathrm{HSSH}) \longrightarrow \mathrm{H_2S} + \frac{1}{8}\,\mathrm{S_8}.$$



Scheme 1.

These results also support the single electron-transfer mechanism. We investigated these reactions by EPR spectroscopy in HMPA, but the signals obtained were too broad to allow us to make their assignment.

Experimental

General. The reagents used were commercial reagent-grade materials except 9-Nitroanthracene and were purified by recrystallization or distillation prior to use. 9-Nitroanthracene was prepared and purified according to the literature.[13] IR spectra were recorded on a Hitachi 295 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a Hitachi R-22 (90 MHz) spectrometer in carbon tetrachloride or deuteriochloroform solution containing tetramethylsilane as an internal standard. Mass spectra were recorded on a Hitachi RMU-6M spectrometer with a direct inlet system, operating at 20 eV. GLC analysis was carried out with a Hitachi 063 gas chromatograph. For column chromatography Wakogel C-300 was used. Products obtained were identified by comparing IR, NMR, MS, GLC, and MP data with those of authentic samples.

Reaction of Benzaldehyde (1) with NaSH in the Presence of Nitrobenzene in Liq. NH_3. A solution of **1** 212 mg (2 mmol), NaSH (98%) 114 mg (2 mmol), and nitrobenzene 31 mg (0.25 mmol) in liq. NH_3 (10 ml) in a titanium autoclave under nitrogen atmosphere was stirred at 40 °C for 5 h. After removal of NH_3, CCl_4 was added to the reaction mixture. The yields of benzyl alcohol (27%), and *N*-benzylideneaniline (9%) and *N,N'*-dibenzylidene-α,α-toluenediamine (5%) were determined by measuring NMR intensities of methylene and methine groups, respectively, using *p*-nitrotoluene as an internal standard in CCl_4 solution. The aqueous solution of residue was extracted with $CHCl_3$. After removal of $CHCl_3$, the residue was separated by silica-gel column chromatography using $CHCl_3$ as an eluent to give benzamide in 25% yield.

Reaction of Substituted Benzaldehydes with NaSH in the Presence of Various Nitro Compounds in Liq. NH_3. A solution of a substituted benzaldehyde (2 mmol), NaSH (98%) 114 mg (2 mmol), and a nitro compound (0.1—2.0 mmol) in liq. NH_3 (10 ml) in a titanium autoclave under nitrogen atmosphere was stirred at 40 °C for 5 h. The reaction mixture was treated as in the case of the reation with nitrobenzene added. Results obtained are summarized in Tables 1 and 2.

Reaction of Benzaldehyde (1) with NaSH in the Presence of a Reductant of Nitrobenzene in Liq. NH_3. A solution of 212 mg (2 mmol), NaSH (98%) 114 mg (2 mmol), and a reductant (2 mmol) in liq. NH_3 (10 ml) in a titanium autoclave under nitrogen atmosphere was stirred at 40 °C for 5 h. After removal of NH_3, CCl_4 was added to the reaction mixture. The yield of benzyl alcohol was determined by measuring the NMR intensity of the methylene group using *p*-nitrotoluene as an internal standard in CCl_4 solution.

Reaction of Nitrobenzene or its Reductants with NaSH in Liq. NH_3. A solution of nitrobenzene or its reductants (nitrosobenzene, phenylhydroxylamine, azoxybenzene, azobenzene, hydazobenzene, or anilne,) (2 mmol), and NaSH (98%) 114 mg (2 mmol) in liq. NH_3 (10 ml) in a titanium autoclave under nitrogen atmosphere was stirred at 40 °C for 5 h. After removal of NH_3, CCl_4 was added to the reaction mixture, and filtered. After removal of CCl_4, the residue was separated by silica-gel column chromatography using $CHCl_3$ as an eluent to give reductants of nitrobenzene. Results obtained are summarized in Table 4.

Reaction of Benzaldehyde (1) with $Na_2S\cdot5H_2O$ in Liq. NH_3. A solution of **1** 212 mg (2 mmol) and $Na_2S\cdot5H_2O$ 336 mg (2 mmol) in liq. NH_3 (10 ml) in a titanium autoclave under nitrogen atmosphere was stirred at 40 °C for 5 h. The reaction mixture was treated similarly to give benzyl alcohol and benzamide in 35 and 37% yield, respectively.

Reaction of Benzophenone with NaSH in the Presence of Azobenzene and Formalin in Liq. NH_3. A solution of benzophenone 364 mg (2 mmol), NaSH (98%) 114 mg (2 mmol), azobenzene 182 mg (1 mmol), and formalin (37%) 162 mg (2 mmol) in liq. NH_3 (10 ml) in a titanium autoclave under nitrogen atmosphere was stirred at 40 °C for 5 h. After removal of NH_3, the reaction mixture was extracted with $CHCl_3$. After removal of $CHCl_3$, the residue was separated by silica-gel column chromatography using $CHCl_3$ as an eluent to give benzhydrol in 27% yield.

Reaction of Benzophenone with $Na_2S\cdot5H_2O$ in the Presence of Formalin in Liq. NH_3. A solutin of benzophenone 364 mg (2 mmol), $Na_2S\cdot5H_2O$ 336 mg (2 mmol), and formalin (37%) 405 mg (5 mmol) in liq. NH_3 (10 ml) in a titanium autoclave under nitrogen atmosphere was stirred at 40 °C for 5 h. Similar treatment of the reaction mixture gave benzhydrol in 58% yield.

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