

and chains. He concluded that the exchange coupling constant decreased as the bridging angle (Cu-X-Cu) decreased. The small bridging angle is anticipated between the pseudotetrahedral copper(II) complex unit. This small bridging angle lead to the small exchange coupling constant between copper(II) ions in $\text{Cu}(\text{dmamt})\text{Cl}_2$.

The pseudotetrahedral geometry around Cu(II) ion in $\text{Cu}(\text{dmamt})\text{Cl}_2$ is supported by the electrochemical properties. Cyclic voltammogram was recorded in 0.1 M TEAP/DMF from -0.5 V to $+1.0$ V vs. Ag/AgCl electrode. $\text{Cu}(\text{dmamt})\text{Cl}_2$ exhibited two cathodic (Epc) and anodic (Epa) peaks at $+0.74$ (Epc), $+0.88$ (Epa) and at $+0.09$ (Epc), $+0.44$ V (Epa). We were tentatively assigned as $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ and $\text{Cu}^{\text{I}}/\text{Cu}^0$ couples, respectively, in the central metal in $\text{Cu}(\text{dmamt})\text{Cl}_2$. The potentials and the peak currents were not changed after scanning several times, indicating that these couples are reversible. In case of CuCl_2 in DMF, the voltammogram obtained in our work is shown only one oxidation-reduction peak at $+0.28$ (Epc) and $+0.64$ (Epa) at the same condition, which might be assigned to $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple. The mid-peak potentials of $\text{Cu}(\text{dmamt})\text{Cl}_2$ were $+0.81$ ($\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$) and $+0.27$ V ($\text{Cu}^{\text{I}}/\text{Cu}^0$). The mid-peak potential of $\text{Cu}(\text{dmamt})\text{Cl}_2$ is somewhat higher than that of $\text{Cu}(\text{sp})\text{Cl}_2$ ($E_{1/2} = +0.60$ for $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ couple in $\text{Cu}(\text{sp})\text{Cl}_2$).⁷ Choi *et al.*⁷ demonstrated that the relatively high reduction potentials of $\text{Cu}(\text{sp})\text{Cl}_2$ was due to the pseudotetrahedral symmetry around the copper(II) ion in $\text{Cu}(\text{sp})\text{Cl}_2$. It is well known that the distortion from square planar to tetrahedral geometry makes the copper(II) ion easier to reduce because of the absence of Jahn-Teller energy.⁸ The mid-peak potentials of $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ in $\text{Cu}(\text{dmamt})\text{Cl}_2$ is also comparable to those of the blue copper proteins ($+0.2$ - $+0.8$ V vs. SHE).⁹ The relatively high reduction potential of the copper proteins has been interpreted as the pseudotetrahedral symmetry around copper(II) site as well as the nature of the donor atoms in the proteins (CuN_2S_2 chromophores).² The similar mid-peak value of $\text{Cu}(\text{dmamt})\text{Cl}_2$ to the copper proteins supports the pseudotetrahedral coordination symmetry around the copper(II) site in $\text{Cu}(\text{dmamt})\text{Cl}_2$, although an x-ray structure determination is necessary for the description of the subject matter.

Experimental

$\text{Cu}(\text{dmamt})\text{Cl}_2$ was prepared by the direct reaction of dmamt and anhydrous CuCl_2 as described in the literature.¹ The brown precipitates were dried in vacuum oven at room temperature. Elemental analysis was performed by the Korea Research Institute of Chemical Technology, Daejeon, Korea. Calculated C; 30.50, H; 4.02, N; 5.08. Found C; 31.15, H; 4.10, N; 5.09.

Magnetic susceptibility measurements were obtained using a Princeton Applied Research vibrating-sample Magnetometer (VSM) operating at field strength of 10 kOe from 4 to 90 K. The magnetometer was calibrated against $\text{HgCo}(\text{NCS})_4$. Finely ground polycrystalline sample weighing 150 mg was housed in precision-milled Lucite sample holder. Temperatures were measured with a calibrated Ga-As diode. The output data were corrected for the diamagnetic of the sample holder and the constituent atoms using Pascals' constants. A value of 60×10^{-6} emu/mol was assumed for the temperature-independent paramagnetism (TIP) of copper(II) ion. Cy-

cllic voltammogram was obtained using a PAR Model 273 Potentiostat in a three electrode configuration and recorded with Kipp & Zenon Model 13 BD XY recorder. The working electrode was a Pt disc electrode (0.38 cm^2) and the counter electrode was a Pt wire. Ag/AgCl electrode was used as a reference electrode. The working solution ($\sim 10^{-3}$ M) was prepared in 0.1M TEAP/DMF as a supporting electrolyte.

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Benzylic Bromination of Alkylbenzenes with Sodium Bromate-Bromotrimethylsilane

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

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Radical halogen substitution of carbon-hydrogen bonds has been considered to be one of the most important reactions for further functionalization. Radical bromination on a benzylic position has been achieved using bromine¹ and *N*-bromosuccinimide.² In addition, bromine complex of styrene-vinylpyridine copolymer,³ bromotrichloromethane,⁴ and copper(II) bromide⁵ were reported to be effective for benzylic bromination. For the majority of brominating agents, the presence of a peroxide or other radical initiator is required.

Recently, we reported that sodium halate-halotrimethylsi-

Table 1. Ratio of Reactants and Products in Toluene Bromination by NaBrO₃/TMSBr

Ratio of Reactants			Ratio of Products			
	TMSBr	NaBrO ₃				Other Brominated Products ^a
1	1.2	0.7	9	84	6	0
1	1.3	0.7	6	70	7	17
1	1.5	0.7	3	81	16	3
1	1.5	1	1	80	13	0
1	2	1	3	87	10	0
1	2	1	9	78	11	2
1	3	1	0	80	20	0

^aRing bromination products and other poly brominated, unidentified products. ^bReaction in the absence of benzyltriethylammonium chloride.

lane systems were very effective for the introduction of halogen atoms on the electron rich aromatic rings.⁶ Sodium bromate, bromotrimethylsilane pair is also effective for the ring bromination of aromatic rings, except for toluenes and other alkylbenzenes.⁶ The bromination using sodium bromate and

bromotrimethylsilane pair took place on the side chain resulting in the formation of benzylic bromides. The benzylic bromination by this reagent pair has been extensively reexamined, and we now report that the benzylic bromination by this reagent system is excellent for the practical introduction of bromine at a benzylic position of alkylbenzenes.

In order to find out appropriate reaction conditions for the optimum mono-bromination of the side chains of toluenes and alkylbenzenes, bromination reactions using the different ratios of bromotrimethylsilane and sodium bromate were examined. For the maximum conversion and minimum polybromination, the 1:2.3:1 molar ratio of toluene, bromotrimethylsilane and sodium bromate turned out to be most effective (Table 1). The reactions were carried out at room temperature in carbon tetrachloride. The presence of 5 mole percent of benzyltriethylammonium chloride helped the dissolution of sodium bromate and shorten the reaction time, although the reaction proceeded well in the absence of it. Other haloalkane solvents can be used instead of carbon tetrachloride.

The optimum reaction conditions for toluene bromination turned out to be appropriate for the bromination of other alkylbenzene derivatives. The results of benzylic bromination of other alkylbenzenes are summarized in Table 2. The reaction proceeded well in the absence of light or a radical initiator, and the amount of the side chain bromination products

Table 2. Benzylic Bromination by NaBrO₃-TMSBr in CCl₄^a

Entry	Alkylbenzene	Reaction		% Conversion ^b	Product Distribution (% Yield)	
		Temp.	Time (hr)		Monobromination	Dibromination
1	toluene	rt	1	97	α -bromotoluene (87)	α,α -dibromotoluene (10)
2	α -bromotoluene	reflux	1	97		α,α -dibromotoluene (95)
2	α -chlorotoluene	reflux	1	95	α -bromo- α -chlorotoluene (93)	
4	ethylbenzene	rt	1	100	α -bromoethylbenzene (97)	
5	butylbenzene	rt	1	100	α -bromobutylbenzene (98)	
6	<i>o</i> -xylene	rt	3	99	α -bromo- <i>o</i> -xylene (85)	α,α' -dibromo- <i>o</i> -xylene (14)
7	<i>p</i> -xylene	rt	2	100	α -bromo- <i>p</i> -xylene (92)	α,α' -dibromo- <i>p</i> -xylene (2)
8	mesitylene	rt	3	85	α -bromomesitylene (60)	α,α -dibromomesitylene (25)
9	1,2,3,4-tetrahydronaphthalene	rt	0.5	100	α -bromo-1,2,3,4-tetrahydronaphthalene (17)	
10	cylohexylbenzene	rt	3	100	α -bromocylohexylbenzene (30)	
11	<i>o</i> -chlorotoluene	rt	4	94	α -bromo- <i>o</i> -chlorotoluene (81)	α,α -dibromo- <i>o</i> -chlorotoluene (13)
12	<i>p</i> -bromotoluene	rt	12	96	α -bromo- <i>p</i> -bromotoluene (84)	α,α -dibromo- <i>p</i> -bromotoluene (12)
13	<i>p</i> -methoxytoluene	rt	1	97	α -bromo- <i>p</i> -methoxytoluene (82)	α,α -dibromo- <i>p</i> -methoxytoluene (15)
14	<i>p</i> -tolunitrile	reflux	20	73	α -bromotolunitrile (70)	α,α -dibromotolunitrile (2)
15	<i>p</i> -nitrotoluene	reflux	20	63	α -bromo- <i>p</i> -nitrotoluene (55)	α,α -dibromo- <i>p</i> -nitrotoluene (8)
16	<i>p</i> -toluenesulfonyl chloride	reflux	20	39	<i>p</i> -bromomethylbenzenesulfonyl chloride (63)	
17	phenylacetic acid	reflux	100	95	α -bromophenylacetic acid (95)	
18	phenylacetaldehyde	reflux	1	100	α -bromophenylacetaldehyde (94)	α,α -dibromophenylacetaldehyde (6)
19	phenylacetone	reflux	60	89	α -bromophenylacetone (89)	
20	<i>o</i> -phthalide	reflux	24	100	α -bromophthalide (5)	α,α -dibromophthalide (93)
21	2-methylnaphthalene	rt	5	100	1-bromo-2-methylnaphthalene (98)	

^aThe reactions were conducted using 1:2:1 ratio of NaBrO₃:TMSBr:substrate in the presence of 5 mol % of benzyltriethylammonium chloride. ^bConsumption of the starting material. ^cOther poly-brominated and ring brominated products were not listed. The difference between % conversion and sum of % yield is regarded to be unidentified or polybrominated products.

did not change even when the reaction was carried out in the dark.

o-Xylene, *p*-xylene, and *p*-methoxytoluene were brominated well and produced the corresponding mono-brominated product in greater than 80% yield. An electron withdrawing group such as cyano, bromo, and nitro on the toluene ring slowed down the reaction rate considerably, but the yield of the corresponding mono-brominated product was satisfactory. The formation of ring brominated product were barely detected in those reactions. *p*-Toluenesulfonyl chloride was partially brominated in refluxing carbon tetrachloride to give *p*-bromomethylbenzenesulfonyl chloride in a moderate yield.

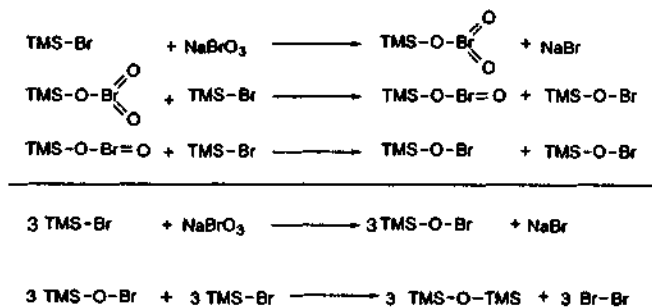
Bromination was successful for benzylic halides. Benzyl bromide and chloride produced exclusively α -brominated products. Phenylacetic acid, phenylacetaldehyde, and phenylacetonitrile were also brominated to produce the corresponding α -bromo compounds in refluxing carbon tetrachloride. The aldehyde moiety was not oxidized and remained intact after 1 hour boiling in carbon tetrachloride. In contrast to the exclusive benzylic bromination of alkylbenzenes, alkyl naphthalenes were brominated mainly on the ring. 2-Methylnaphthalene, for example, was ring brominated, and 1-bromo-2-methylnaphthalene was the only brominated product in this reaction.

In the bromination of alkylbenzenes of longer linear alkyl chains, the initial bromination product usually undergo β -elimination leading to an olefin and subsequent bromine addition resulted in polybrominated products.³ This type of side reactions were suppressed significantly in our procedure producing benzylic bromides in satisfactory yields. Thus 1-bromo-1-phenylethane, 1-bromo-1-phenylbutane were produced from the corresponding alkylbenzenes. However, phenylcyclohexane and 1,2,3,4-tetrahydronaphthalene produced only a small amount of α -monobromo compound together with a mixture of complicated bromination products.

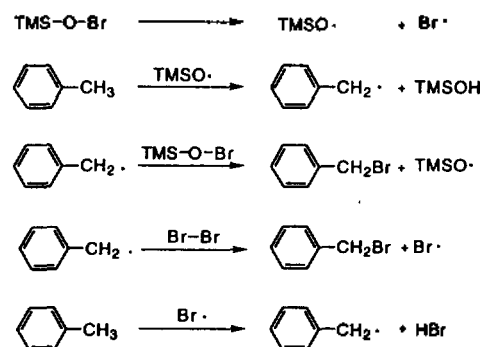
The present procedure does not apply to the allylic bromination of cyclic and acyclic olefins. Addition of bromine across the carbon-carbon double bonds was the main reaction path. Cyclohexene and 1-octene produced 1,2-dibromocyclohexane and 1,2-dibromooctane in better than 90% yield.

Although oxidation of acyloins⁷ and bromination of certain aromatic rings in sulfuric acid media were reported,⁸ bromate salts, unlike bromites,⁹ are not powerful oxidants and rarely used for the oxidation or bromination reactions of organic functional groups. Some inorganic compounds were easily oxidized by sodium bromate, and it has been often used as a co-oxidant for ceric ammonium nitrate,¹⁰ ceric sulfate¹¹ and ruthenium tetrachloride.¹¹

The formation of active brominating species from bromotrimethylsilane and sodium bromate resembles the formation of bromine from the reaction of sodium bromate and sodium bromide in acetic acid.¹² Sodium bromate is believed to react with bromotrimethylsilane to produce initially trimethylsilyl bromate. This bromate ester sequentially oxidizes two more equivalents of bromotrimethylsilane to trimethylsilyl hypobromite. During the process, the bromate ester is reduced to trimethylsilyl hypobromite. Trimethylsilyl hypobromite eventually reacts with another mole of bromotrimethylsilane forming hexamethyldisiloxane and bromine. Bromine formation was actually observed and hexamethyldisiloxane was another end product of the reaction. The sequential reactions



Scheme 1. Generation of reactive brominating agents from NaBrO₃/TMSBr.



Scheme 2. Initiation and chain propagation steps in radical bromination by NaBrO₃/TMSBr.

leading to the generation of bromine is given in Scheme 1.

Since bromine alone is not effective for radical benzylic bromination in the absence of light or radical initiators, the bromine species of intermediate oxidation state is believed to play an important role for the side chain bromination of toluenes. One possibility is the homolytic self-dissociation of oxygen-bromine bond of intermediate trimethylsilyl hypobromite. The trimethylsilyloxy radical can abstract a benzylic hydrogen and initiate a series of radical bromination. A part of trimethylsilyl hypobromite is consumed for the production of bromine. The benzyl radical abstracts bromine atom either from bromine or trimethylsilyl hypobromite. The proposed mechanism for benzylic bromination by bromine or trimethylsilyl hypobromite is given in Scheme 2.

Experimental Section

Toluene analogs and other alkylbenzenes were purchased from Aldrich Chemical Co. and were used without further purification. Bromotrimethylsilane was prepared by distilling the mixture of hexamethyldisiloxane and phosphorous tribromide according to the known procedure.¹³ NMR spectra were recorded either on a Varian Gemini-200 (200 MHz) or Varian EM-360A (60 Mhz) spectrometer using deuteriochloroform as a solvent. IR spectra were recorded with a Perkin Elmer 1330 IR spectrometer neat or as potassium bromide pellets. Gas chromatographic analysis of various halogenated products was carried out on a Hewlett-Packard 5880A with a flame ionization detector. Coiled fused-silica

capillary columns of 10 or 25 m in length, 0.53 mm in inner diameter, 2.56 or 1.33 micrometer in film thickness were used. Aluminum-backed cut sheets of Merck Kieselgel 60 PF₂₅₄ were used for TLC, and Merck Kieselgel 60 (70-230 mesh ASTM) was used for column chromatographic separation and purification of products.

Bromination of toluene with TMSBr-NaBrO₃. Toluene (184 mg, 2 mmol) was dissolved in 6 mL of CCl₄. Sodium bromate (302 mg, 2 mmol) and benzyltriethylammonium chloride (22 mg, 0.1 mmol) were added. To the stirring reaction mixture bromotrimethylsilane (615 mg, 4 mmol) dissolved in 2 mL of CCl₄ was added. The resulting mixture was stirred at ambient temperature for a designated period of time or until the TLC showed a complete consumption of toluene. Insoluble salts were filtered off, and the low boiling components were evaporated. The crude product was analyzed by GC or NMR. The product distributions from other reactions are listed in Table 2.

Preparative procedure. A substrate (0.1 mol) was dissolved in 40 mL of CCl₄. Sodium bromate (15 g, 0.1 mol) and benzyltriethylammonium chloride (150 mg) were added. To the stirring reaction mixture bromotrimethylsilane (30 g, 0.2 mol) dissolved in 10 mL of CCl₄ was added from a dropping funnel over a period 5-10 min. The resulting mixture was stirred at ambient temperature for a designated period of time or until the TLC showed a complete consumption of the substrate. The reaction mixture was poured into 300 mL of ice-cold water. The products were extracted with 15 mL of CCl₄ twice and the combined extracts were washed with water, dried over anhydrous MgSO₄. The filtrate was concentrated and the residue was either distilled or recrystallized. 1-Bromo-1-phenylethane was obtained in 90% yield after distillation. The isolated yields of the products were slightly lower than those by chromatography.

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Synthesis of Symmetric 3,6-Disubstituted-1,2,4,5-Tetrazines using an Activated Catalyst Prepared by the Reaction of Copper Nitrate with Excess Zinc in the Presence of Hydrazine Monohydrate

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Since the first symmetric 3,6-disubstituted-1,2,4,5-tetrazine derivatives **2**¹ were prepared by the dimerization of ethyl diazoacetate, several different routes to symmetric and unsymmetric 3,6-disubstituted-1,2,4,5-tetrazines have been described including the treatment of hydrazine with iminoethers,² iminoesters,³ thioamides,⁴ selenoesters,⁵ selenoamides,⁵ imidates,⁶ amidines,⁷ dichloroazines,⁸ hydrazonoyl chlorides,⁹ fluoroolefines,¹⁰ and chloroformylhydrazone.¹¹

Even though direct synthesis of 1,2,4,5-tetrazines from a cyano group could be the best method, only a few examples have been previously reported in the literature.¹² For example, Abdel-Rahman^{12c} reported direct synthesis of tetrazine by the action of hydrazine monohydrate-sulphur mixture on various nitriles. However, we and others^{7a} found that treatment of benzyl cyanide with sulphur-hydrazine hydrate gave 4-amino-3,5-dibenzyl-1,2,4-triazole,¹³ not 3,6-diphenyl-dihydro-1,2,4,5-tetrazine. In the case of benzonitrile, we isolated the corresponding dihydrotetrazine which is readily oxidized in air to the red-colored 3,6-diphenyl-1,2,4,5-tetrazine. Similarly with acetonitrile, the product was not 3,6-dimethyl-dihydro-1,2,4,5-tetrazine but 4-amino-3,5-dimethyl-1,2,4-triazole.¹³

Zajac *et al.*^{12d} also reported a direct synthesis of 3,6-disubstituted-1,2,4,5-tetrazines from cyano compounds with Raney nickel-hydrazine monohydrate under reflux with ethanol. However, only 2-cyanopyridine and 4-cyanopyridine were illustrated.

We recently reported that activated metal powders prepared from the reaction of copper(II) sulfate or nickel chloride with excess zinc and hydrazine monohydrate in dry ethanol under reflux easily reduces nitroarenes to the corresponding amino compounds in high yields.¹⁴⁻¹⁵ We also reported that