J. Org. Chem. **1998,** *63,* 6023−6026

An Alternative Method for the Selective Bromination of Alkylbenzenes Using $NaBrO_3/NaHSO_3$ Reagent

Daisuke Kikuchi, Satoshi Sakaguchi, and Yasutaka Ishii*

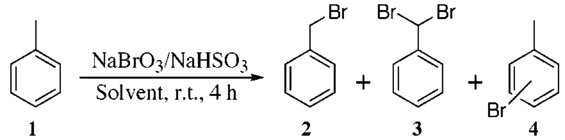
Department of Applied Chemistry, Faculty of Engineering and High Technology Research Center, Kansai University, Suita, Osaka 564-8680, Japan

Received December 15, 1997

α-Brominated alkylbenzenes are a valuable class of compounds in organic synthesis, since they are frequently used as the starting materials for synthesis of a wide variety of important compounds. α-Bromination of alkylbenzenes is usually performed by the use of bromine,[1] NBS,[2] $CBrCl_3$,[3] $CuBr_2$,[4] and Br^-/CAN[5] under heating or irradiation of light. To achieve the bromination by these reagents in satisfactory yields, the reaction must be carried out in halogenated solvents such as CCl_4, $CHCl_3$, and CH_2ClCH_2Cl. However, these solvents will become difficult to use from an environmental point of view. In this respect, Shaw et al. have recently demonstrated the free-radical bromination of toluene and xylenes with bromine in water under irradiation of a mercury lamp.[6]

In previous papers, we showed that $NaBrO_3$ combined with a reducing reagent such as $NaHSO_3$ ($NaBrO_3/NaHSO_3$) generates in situ hypobromous acid (HOBr) and serves as an effective bromohydroxylation reagent of olefins,[7] alkynes, and allylic alcohols[8] and an oxidizing agent of primary alcohols,[9] diols, and ethers.[10] In the course of our study to extend the scope of the $NaBrO_3/NaHSO_3$ reagent in organic synthesis, we have found that this reagent facilitates the α-bromination of alkylbenzenes under a two-phase system using ethyl acetate as solvent under ambient conditions. In this paper, we wish to report the selective side chain and ring brominations[11] of alkylbenzenes with the $NaBrO_3/NaHSO_3$ reagent.

Table 1. Bromination of Toluene with $NaBrO_3/NaHSO_3$ Reagent under Several Conditions[a]



1 **2** **3** **4**

Run	Solvent	Conv. (%)	Yield / %		
			2	**3**	**4**
1	$AcOEt/H_2O$	>99	72	22	trace
2 [b]	$AcOEt/H_2O$	52	47	trace	trace
3	$c\text{-}C_6H_{12}/H_2O$	>99	67	18	trace
4	$(i\text{-}Pr)_2O/H_2O$	30	20	2	trace
5 [c]	H_2O	81	51	10	6
6 [c]	CH_3CN/H_2O	>99	5	2	57(68/32)[d]
7 [c]	$t\text{-}BuOH/H_2O$	74	7	1	53(70/30)[d]

[a] To a solution of alkylbenzene (3 mmol) in organic solvent (6 mL) and $NaBrO_3$ (9 mmol) in water (4.5 mL) was added dropwise $NaHSO_3$ (9 mmol) in H_2O (9 mL) during a period of 15 min at room temperature. [b] $NaBrO_3/NaHSO_3$ (3/3 mmol) was used. [c] A small amount of aromatic bromination products derived from **2** and **4** were formed. [d] Ratio of ***o*-4/*p*-4**.

The bromination of toluene (**1**) by the $NaBrO_3/NaHSO_3$ reagent was chosen as a model reaction and carried out under various reaction conditions. Representative results are shown in Table 1.

To a two-phase system comprised of ethyl acetate involving **1** and aqueous $NaBrO_3$ (3 equiv) was added dropwise aqueous $NaHSO_3$ (3 equiv) over a period of about 15 min under stirring and the mixture was allowed to react at room temperature for 4 h. The reaction produced α-bromotoluene (**2**) in 72% yield along with α,α′-dibromo toluene (**3**) (22%) (run 1). When **1** was allowed to react with a stoichiometric amount of $NaBrO_3/NaHSO_3$ (1 equiv), **2** was formed in unsatisfactory yield (47%) (run 2). Hence, the reaction was carried out by the use of 3 equiv of $NaBrO_3/NaHSO_3$. Similarly, the reaction of **1** using cyclohexane as solvent in place of ethyl acetate produced **2** as the major product (run 3). No bromination of the cyclohexane used as the solvent was observed. It is important to note that the side bromination of **1** can be successfully carried out using $NaBrO_3/NaHSO_3$ reagent in ethyl acetate or cyclohexane as the solvent, since the conventional bromination of alkylbenzenes under irradiation is usually conducted in environmentally unfavorable halogenated hydrocarbon. The reaction in a mixed solvent of diisopropyl ether and water led to **2** in low conversion (30%) and yield (20%) (run 4). This is because the diisopropyl ether itself was oxidized by this

---

(1) (a) Snell, J. M.; Weissherger, A. *Organic Synthesis*; John Wiley: New York, 1955; Collect. Vol. III, p 788. (b) Stephenson, E. F. M. *Organic Synthesis*; John Wiley: New York, 1963; Collect. Vol. III, p 984. (c) Quertani, M.; Girard, P.; Kagan, H. B. *Bull. Chem. Soc. Chim. Fr.* II, **1982**, 327. (d) Sket, B.; Zupen, M. *J. Org. Chem.* **1986**, *51*, 929. (e) Venkatachalapathy, C.; Pitchumani, K. *Tetrahedron* **1997**, *53*, 2581.

(2) (a) Djerassi, C. *Chem. Rev.* **1948**, *43*, 271. (b) Wenner, W. *J. Org. Chem.* **1952**, *17*, 523. (c) Wenner, W. *Angew. Chem.* **1959**, *71*, 349. (d) Andrews, L. J.; Keefer, R. M. *J. Org. Chem.* **1969**, *34*, 944. (e) Lind, J. Jonsson, M.; Xinhua, S.; Eriksen, T. E.; Eberson, L. *J. Am. Chem. Soc.* **1993**, *115*, 3503. (f) Carreno, M. C.; Ruano, J. L. G. *J. Org. Chem.* **1995**, *60*, 5328.

(3) (a) Huyser, E. S. *J. Chem. Soc.* **1960**, 391. (b) Hori, Y.; Nagano, Y.; Uchiyama, H.; Yamada, Y.; Taniguchi, H. *Chem. Lett.* **1978**, 73. (c) Jon, A. O. *J. Org. Chem.* **1966**, *31*, 4933.

(4) Chaintreau, A.; Adrian, G.; Couturier, D. *Synth. Commun.* **1981**, 669.

(5) Baciocchi, E.; Rol, C.; Sebstiani, G.; Serena, B. *J. Chem. Res.* **1984**, 24.

(6) Show, H.; Perlmutter, H. D.; Gu, C. *J. Org. Chem.* **1997**, *62*, 236.

(7) Previously, an appropriate method for generating HOBr or HOI equivalents from $NaBrO_3$ or $NaIO_4$ combined with various reducing agents ($NaHSO_3$, Na_2SO_3, $Na_2S_2O_3$, Na_2HPO_3, $FeSO_4$, and $H_2C_2O_4$ etc.) was examined, and the $NaHSO_3$ was found to be the best reducing reagent employed: Ohta, H.; Sakata, Y.; Takeuchi, T.; Ishii, Y. *Chem. Lett.* **1990**, 733.

(8) Masuda, H.; Takase, K.; Nishio, M.; Hasegawa, A.; Nishiyama, Y.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **1994**, *59*, 5550.

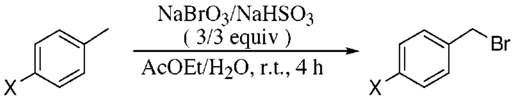
(9) Takase, K.; Masuda, H.; Kai, O.; Nishiyama, Y.; Sakaguchi, S.; Ishii, Y. *Chem. Lett.* **1995**, 871.

(10) Sakaguchi, S.; Kikuchi, D.; Ishii, Y. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2561.

(11) For ring brominations, various papers have appeared: (a) Mckillop, A.; Bromley, D. *J. Org. Chem.* **1972**, *37*, 88. (b) Mitchell, R. H.; Williams, R. V. *J. Org. Chem.* **1979**, *44*, 4733. (c) Bovonsombat, P.; Mcnelis, E. *Synthesis* **1993**, 237. (d) Srivastava, S. K.; Bhaduri, A. P.; Man, D.; Chanhan, S. *J. Chem. Soc., Chem. Commun.* **1996**, 2679. (e) Bezodis, P.; Hanson, J. R.; Philippe, P. *J. Chem. Res.* **1996**, 334.(f) Clark, J. H.; Ross, J. C.; Macquarrie, D. J.; Barlow, S. J.; Bastock, T. W. *J. Chem. Soc., Chem. Commun.* **1997**, 1203. (g) Vega, F.; Sasson, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 653. (h) Smith, K.; Bahzad, D. *J. Chem. Soc., Chem. Commun.* **1996**, 467.

S0022-3263(97)02263-9 CCC: $15.00

Table 2. Bromination of *p*-Substituted Toluenes with $NaBrO_3/NaHSO_3$ Reagent[a]

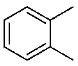
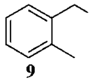
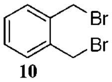
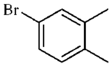
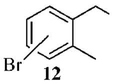
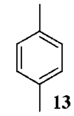
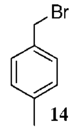
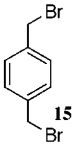
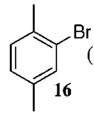
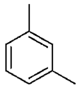
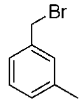
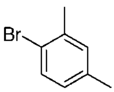


5a - 5d **6a - 6d**

Run	Substrate (X =)	Conv. (%)	Product[c] (Yield / %)
1	Cl (**5a**)	97	**6a** (74)
2	Br (**5b**)	98	**6b** (76)
3	COOH (**5c**)	96	**6c** (80)
4	*t*-Bu (**5d**)	97	**6d** (63)
5[b]	**5d**	97	**6d** (2) **7** (84)[d]

[a] To a solution of alkylbenzene (3 mmol) in ethyl acetate (6 mL) and $NaBrO_3$ (9 mmol) in water (4.5 mL) was added dropwise $NaHSO_3$ (9 mmol) in H_2O (9 mL) during a period of 15 min at room temperature. [b] Reaction was carried out in CH_3CN (6 mL) for 2 h. [c] Isolated yield. [d] Yield of 2-bromo-*p*-*tert*-butyltoluene (**7**).

Table 3. Bromination of Xylenes with $NaBrO_3/NaHSO_3$ Reagent[a]

Run	Substrate	Solvent	Conv. (%)	Product (Yield / %)	
1[b]	 **8**	AcOEt/H_2O	85	 (71)[d] **9**	 (6) **10**
2[c]	**8**	AcOEt/H_2O	>99	**9** (13)	**10** (70)[d]
3	**8**	CH_3CN/H_2O	>99	 (51)[d] **11**	 (11) **12**
4	 **13**	AcOEt/H_2O	>99	 (59) **14**	 (39) **15**
5[c]	**13**	AcOEt/H_2O	>99	**14** (6)	**15** (70)[d]
6	**13**	CH_3CN/H_2O	>99	**14** (<1)	 (62)[d] **16**
7	 **17**	AcOEt/H_2O	>99	 (20) **18**	 (34) **19**
8	**17**	$c\text{-}C_6H_{12}/H_2O$	>99	**18** (64)[d]	**19** (1)
9	**17**	CH_3CN/H_2O	83	**18** (<1)	**19** (57)[d]

[a] To a solution of alkylbenzene (3 mmol) and $NaBrO_3$ (9 mmol) in organic solvent/water (6/4.5–6 mL) was added dropwise $NaHSO_3$ (9 mmol) in H_2O (4.5–12 mL) over a period of 15 min at room temperature, and the mixture was stirred for 4 h. [b] Stirring for 1 h. [c] $NaBrO_3/NaHSO_3$ (12/12 mmol) was used. [d] Isolated yield.

reagent.[10] The reaction of **1** without an organic solvent proceeded with somewhat lower selectivity to form **2** and **3** as well as *o*- and *p*-bromotoluenes (*o*-**4** and *p*-**4**) (run 5). α-Bromotoluene, **2**, may be formed by the reaction of **1** with a bromine radical ($Br^\bullet$) liberated from the $NaBrO_3/NaHSO_3$ reagent as discussed later.

In contrast to the bromination using the two-phase system, the bromination of **1** with the $NaBrO_3/NaHSO_3$ reagent under homogeneous conditions using acetonitrile or *tert*-butyl alcohol as the solvent resulted in ring-brominated products *o*-**4** and *p*-**4** as major products (runs 6 and 7). The *o*-**4**/*p*-**4** ratio obtained here was close to that observed in the reaction with $HOBr/HClO_4$.[12] The ring bromination of **1** under the homogeneous system may be caused by a positive ionic species derived from the $NaBrO_3/NaHSO_3$ reagent, as discussed later.

On the basis of these results, a variety of para-substituted toluenes were allowed to react with the $NaBrO_3/NaHSO_3$ reagent under two-phase and homogeneous systems (Table 2).

p-Chloro- and bromobenzenes, **5a** and **5b**, were reacted with $NaBrO_3/NaHSO_3$ (3 equiv) in ethyl acetate/water at room temperature for 4 h to form the corresponding α-bromotoluenes, **6a** and **6b**, in good yields (runs 1 and 2). Similarly, *p*-methylbenzoic acid (**5c**) was converted into *p*-(α-bromomethyl)benzoic acid (**6c**) in excellent yield (80%) (run 3). However, *p*-*tert*-butyltoluene (**5d**) under these conditions gave *p*-*tert*-butyl(α-bromo)toluene in somewhat low yield (63%) (run 4). When the same reaction was carried out in aqueous acetonitrile for 2 h, the bromination on the aromatic ring took place with high selectivity to give 2-bromo-*p*-*tert*-butyltoluene (**7**) in 84% yield along with **6d** (2%).

Table 3 shows the results for the bromination of xylenes with $NaBrO_3/NaHSO_3$ (3 equiv) in ethyl acetate/water and in aqueous acetonitrile.

o-Xylene (**8**) was more reactive than toluene **1** to afford α-bromo- and α,α′-dibromo-*o*-xylenes, **9** and **10**, in 71% and 6% yields, respectively, within 1 h (run 1). The reaction of **8** using 4 equiv of $NaBrO_3/NaHSO_3$ reagent produced **10** in satisfactory yield (70%) (run 2). Under homogeneous conditions using acetonitrile as the solvent, the bromination at the aromatic ring of **8** occurred to form 4-bromo-*o*-xylene (**11**) (51%) and a small amount of dibromo compound **12** (11%) (run 3). *p*-Xylene (**13**) was likewise brominated in ethyl acetate to afford α-bromo- and α,α′-dibromo-*p*-xylenes, **14** and **15** (run 4). When **13** was reacted with 4 equiv of the reagent, dibromoxylene **15** was obtained as the principal product (70%) (run 5). As expected, in acetonitrile, **13** gave 2-bromo-*p*-xylene (**16**) (62%) (run 6). In the case of *m*-xylene (**17**), the reaction took place with somewhat more difficulty than those of *o*- and *p*-xylenes, **8** and **13**, to form a mixture of side-chain- and ring-brominated products, α-bromo-*m*-xylene (**18**) and 4-bromo-*m*-xylene (**19**), respectively, in low yields. However, the selectivity of the side-chain bromination was found to be considerably improved when cyclohexane was used as the solvent instead of ethyl acetate. Thus, the reaction of **17** in cyclohexane/water produced **18** in higher selectivity (64%) with a very small amount of **19** (1%) (run 8).

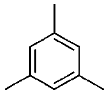
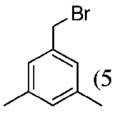
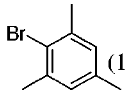
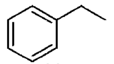
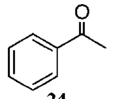
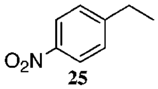
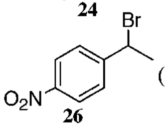
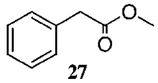
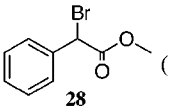
Table 4 shows the bromination of various alkylbenzenes with the $NaBrO_3/NaHSO_3$ reagent under the two-phase system.

Mesitylene (**20**) was brominated to α-bromomesitylene (**21**) in 50% yield together with bromomesithylene (11%) (run 1). It is noteworthy that the side bromination of **20** by $NaBrO_3/NaHSO_3$ can be achieved by using the two-phase system consisting of cyclohexane and water, since the bromination of **20** is reported to take place at the aromatic ring rather than the side chain, even under irradiation conditions.[6] Hence, the present bromination method using $NaBrO_3/NaHSO_3$ is considered to be a

---

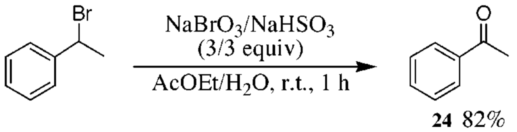
[12] Stocik, L. M.; Brown, H. C. *Advanced Physical Organic Chemistry*; Gold, V., Ed.; Academic Press: New York, 1963; Vol. 1, p 35.

Table 4. Bromination of Various Alkylbenzenes with $NaBrO_3/NaHSO_3$ Reagent[a]

Run	Substrate	Time (h)	Conv. (%)	Product (Yield / %)
1[b]	 **20**	4	97	 **21** (50)[c]  **22** (11)
2	 **23**	4	80	 **24** (51)
3	 **25**	7	>99	 **26** (85)[c]
4	 **27**	6	>99	 **28** (86)[c]

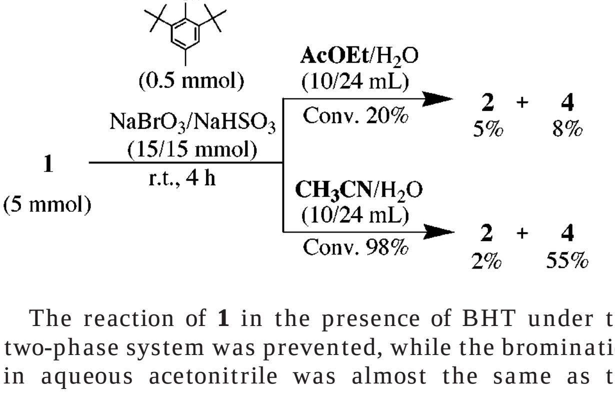
[a] To a solution of alkylbenzene (3 mmol) and $NaBrO_3$ (9 mmol) in ethyl acetate/water (6/4.5 mL) was added dropwise $NaHSO_3$ (9 mmol) in H_2O (9 mL) during a period of 15 min at room temperature, and the mixture was stirred. [b] In cyclohexane/water (6/4.5 mL) at 50 °C. [c] Isolated yield.

useful tool for the bromination of **20** to **21**. Ethylbenzene (**23**) resulted in acetophenone (**24**) (51%) rather than the corresponding α-brominated compound (run 2). The **24** is believed to be formed through (α-bromo)ethylbenzene. Indeed, (α-bromo)ethylbenzene prepared independently was reacted with $NaBrO_3/NaHSO_3$ to afford **24** in good yield (82%) (eq 1). Unlike **23**, *p*-nitroethylbenzene (**25**) and methyl phenyl acetate (**27**) under these conditions produced α-bromo-*p*-nitrobenzene (**26**) (85%) and α-bromophenyl acetate (**28**) (86%), respectively, in good yields (runs 3 and 4).



(1)

To obtain information on the brominating species by the $NaBrO_3/NaHSO_3$ reagent in both systems, we examined the reaction of **1** with $NaBrO_3/NaHSO_3$ in the presence of 2,5-di-*tert*-butyl-*p*-cresol (BHT), which serves as the radical scavenger (eq 2).



(2)

The reaction of **1** in the presence of BHT under the two-phase system was prevented, while the bromination in aqueous acetonitrile was almost the same as the bromination without BHT to give ring-brominated products, *o*-**4** and *p*-**4**. This indicates that the free-radical bromination by Br• does occur in ethyl acetate and the ring-bromination by Br^+ occurs in aqueous acetonitrile.

Next, we examined the bromination of **1** using Br_2 in place of $NaBrO_3/NaHSO_3$ reagent under these conditions (eq 3). In contrast to the bromination of **1** by $NaBrO_3/NaHSO_3$ in $AcOH/H_2O$, where the side bromination of **1** took place in high selectivity to give α-bromotolune **2** (Table 1, run 1), the bromination by Br_2 under the same conditions resulted in the ring-brominated product, **4**, rather than the side-brominated product, **2**, in low yield. The behavior of these brominating agents is quite different from each other.

$$\underset{(5\ \text{mmol})}{\mathbf{1}} + \underset{(15\ \text{mmol})}{Br_2} \xrightarrow[\text{r.t., 4 h}]{} \mathbf{2} + \mathbf{4} \quad (3)$$

Solv. (mL)	Yield (%)	
	2	**4**
$AcOEt/H_2O$ (10/24)	13	27
CH_3CN/H_2O (10/24)	2	73

Owing to the difficulty of isolating any brominating species derived from $NaBrO_3/NaHSO_3$ reagent in $AcOEt/H_2O$ and the complexity of the reaction medium employing the two-phase system, it seems rather hazardous to make an accurate assessment about the nature of the brominating species involved in this reaction, However, we can make several proposals which seem to agree with the experimental results. Previously, we showed that the $NaBrO_3/NaHSO_3$ reagent is a good source for obtaining hypobromous acid, HOBr, and that the treatment of alkenes with the $NaBrO_3/NaHSO_3$ reagent in aqueous acetonitrile produced the corresponding bromohydrines in good yields.[8] Hence, the reaction is initiated by the generation of HOBr from $NaBrO_3/NaHSO_3$ in the aqueous phase, and then the resulting HOBr is thought to decompose gradually in aqueous solution with liberation of Br• or a Br• equivalent, which moves from the aqueous phase to the ethyl acetate phase, in which the substrate **1** is dissolved. As a consequence, the side-chain bromination of **1** takes place preferentially in $AcOEt/H_2O$ system to form **2** in preference to **4**.

On the other hand, under homogeneous conditions using aqueous acetonitrile, the attacking entity in the bromination of **1** by $NaBrO_3/NaHSO_3$ probably a cationic bromine species such as HOBr or H_2OBr^+, in which H_2O is a carrier of Br^+. Indeed, the ring bromination of **1** by the Br^+ generated from HOBr under acidic conditions is reported to produce *o*-**4** in preference to *p*-**4**,[12] in contrast to that by the polarized bromine molecule (Br_2), which produces predominantly *p*-**4** over *o*-**4**.[13,14] Under these conditions, toluene **1** is thought to be easily subjected to the electrophilic substitution by Br^+ to lead to *p*-bromotoluene **4** as the principal product. However, since an ionic species such as HOBr barely exists in ethyl acetate dissolved an alkylbenzene, no ring bromination based on Br^+ occurs under such conditions.

---

(13) (a) Furuya, Y.; Morita, A.; Urasaki, I. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 997. (b) Derbyshire, D. H.; Waters, W. A. *J. Chem. Soc.* **1950**, 573. (c) Branch, S. J.; Jones, B. *J. Chem. Soc.* **1954**, 2317. (d) Mare, P. B. D.; Harvey, J. T. *J. Chem. Soc.* **1957**, 131. (e) Mare, P. B. D.; Harvey, J. T. *J. Chem. Soc.* **1957**, 923. (f) Mare, P. B. D.; Harvey, J. T. *J. Chem. Soc.* **1956**, 36. (g) Mare, P. B. D.; Hilton, I. C. *J. Chem. Soc.* **1962**, 997. (h) Ridd, J. H. *J. Chem. Soc., Perkin. Trans. 2* **1973**, 1321.(i) Harrison, J. J.; Pellegrini, J. P.; Selwittz, C. M. *J. Org. Chem.* **1981**, *46*, 2169.

(14) de la Mare, P. B. O.; Harvey, J. T. *J. Chem. Soc.* **1956**, 36.

In conclusion, we developed a new α-brominating method of alkylbenzenes with $NaBrO_3/NaHSO_3$ using nonhalogenated solvents under mild conditions. This method provides an alternative, facile α-bromination of alkylbenzenes, since $NaBrO_3$ is cheap, nontoxic, stable, and easy to handle compared with liquid bromine. In addition, it was found that the regioselectivity in the side chain or ring bromination of alkylbenzenes can be easily controlled by choosing the reaction conditions, either a two-phase or a homogeneous system.

Experimental Section

General Procedures. All starting materials were commercially available. GC analysis was performed with a flame ionization detector using a 0.2 mm × 25 m capillary column (OV-1, OV-17). ^{1}H and ^{13}C NMR were measured at 270 and 67.5 MHz, respectively, in $CDCl_3$ with Me_4Si as the internal standard. Infrared (IR) spectra were measured using NaCl plates. GC−MS spectra were obtained at an ionization energy of 70 eV. The yields of products were estimated by isolation by column chromatography and from the peak areas based on the internal standard technique.

Side-Chain Bromination of Alkylbenzenes with $NaBrO_3$/$NaHSO_3$ Reagent. To a solution of $NaBrO_3$ (1.35 g, 9 mmol) in water (4.5 mL) was added alkylbenzenes (3 mmol) in ethyl acetate (6 mL), followed by a solution of $NaHSO_3$ (0.93 g, 9 mmol) in water (9 mL) over a period of about 15 min, and the mixture was stirred at room temperature for 4 h. The mixture was poured into 50 mL of ether. After separation of the phases, the aqueous layer was extracted twice with ether, and the combined organic layer was washed with anhydrous $Na_2S_2O_3$ solution and dried over $MgSO_4$. The solvents were then removed in vacuo, and the residue was purified by column chromatography (silica gel, hexane:ethyl acetate = 10:1) to give α-brominated product.

Aromatic Ring Bromination of Alkylbenzenes with $NaBrO_3$/$NaHSO_3$ Reagent. To a solution of $NaBrO_3$ (1.35 g, 9 mmol) in water (4.5 mL) was added alkylbenzenes (3 mmol) in acetonitrile (6 mL), followed by a solution of $NaHSO_3$ (0.93 g, 9 mmol) in water (9 mL) over a period of about 15 min, and the mixture was stirred at room temperature for 4 h. The products were isolated by the same method as described above.

Bromination of Alkylbenzenes with Br_2. To a solution of **1** (3 mmol) in acetonitrile or ethyl acetate (10 mL) and water (24 mL) in water (4.5 mL) was added Br_2 (1.20 g, 15 mmol), and the mixture was stirred at room temperature for 4 h. The yields of products were estimated from the peak areas on the basis of the internal standard technique. In the bromination of **1** using ethyl acetate as the solvent, approximately 40% of **1** was recovered unchanged.

Compounds **2**−**4**, **6b**,**c**,**d**, **9**−**11**, **14**−**16**, **18**, **19**, **22**, **24**, **26**, and **28** are commercially available from Aldrich and were identified through comparison of the isolated products with authentic samples. Compound **6a** is commercially available from Tokyo Kasei Co Ltd.

2-Bromo-4-*tert*-butyltoluene (7).[15] ^{1}H NMR δ 7.53 (d, J = 1.62 Hz, 1H), 7.15−7.20 (m, 2H), 7.35 (s, 3H), 1.29 (s, 9H); ^{13}C NMR δ 150.7, 134.6, 130.3, 129.3, 124.7, 124.3, 34.4, 31.2, 22.2; IR (NaCl) 2963, 2873, 1496, 1384, 1250, 1037, 818 cm^{-1}.

4-Nitro-(1-bromoethyl)benzene (26):[16] ^{1}H NMR δ 8.19 (d, J = 8.91 Hz, 2H), 7.60 (d, J = 8.91 Hz, 2H), 5.21 (q, J = 7.02 Hz, 1H), 2.05 (d, J = 7.02 Hz, 3H); ^{13}C NMR δ 149.9, 147.4, 127.7, 123.8, 46.4, 26.3; IR (NaCl) 2978, 2353, 1605, 1519, 1347, 1180, 858 cm^{-1}.

Acknowledgment. This work was partly supported by the Private University Fund.

Supporting Information Available: Copies of ^{13}C NMR and ^{1}H NMR spectra for the compounds **6a**,**b**, **7**, **9**, **10**, **14**, **15**, **18**, **19**, **22**, and **26** (22 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO972263Q

---

(15) Yamato, T.; Matsumoto, J.; Ide, S.; Tokuhisa, K.; Suehiro, K.; Tahsiro, M. *J. Org. Chem.* **1992**, *57*, 5243.

(16) Kozuka, S.; Nakamura, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2407.