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BROMINATION OF AROMATIC MOLECULES WITH POLYMER SUPPORTED REAGENTS[1]

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Abstract - Crosslinked co-poly/styrene-4-vinyl(N-hexylpyridinium bromide) was converted with bromine or chlorine to insoluble polymer supported complexes 1 or 2 respectively, and their reactivity studied in reactions with various aromatic molecules. Reagent 1 was found in all cases to be milder than reagent 2 and regiospecifically transformed alkoxy and amino substituted benzenes (3) into 4-bromo derivatives, while corresponding reactions with 2 resulted in dibromo derivatives. Several benzoheterocyclic molecules were converted with 1 to substitution or addition products, i.e. 2,3-dibromo-N-methylpyrrole, 3-bromobenzo/b/thiophene, and 2,3-dibromo-2,3-dihydrobenzofuran. In the series of ortho-alkyl disubstituted benzene derivatives, i.e. o-xylene, indane, and tetraline, where the Mills-Nixon effect was established with various electrophilic reagents, bromination reactions with 2 showed higher β-selectivity than the corresponding reactions with bromine. The rate of bromination in various alkyl substituted benzenes with reagent 2 depended on the magnitude of the alkyl group, as well as the para/ortho regioselectivity, amounting to 100% in the case of tert-butylbenzene.

Bromination of aromatic and heteroaromatic molecules has been widely investigated and various reagents are convenient; however, their choice depends strongly on the structure of the organic molecules and the functional groups present[2]. It has been demonstrated that introduction of bromine into organic molecules is also possible with polymer supported reagents[3-10]. The chemical reactivity of the reagent attached to the polymer backbone can be changed, which demands a detailed study of the effect of the polymer support, reaction conditions, and the structure of the organic molecule[11].

We have found[1] that various co-poly/styrene-4-vinyl(N-alkylpyridinium bromides)/ can be converted with chlorine to new insoluble polymeric reagents, which proved to be able to convert olefins to vicinal bromochlorides and iso-propyl benzene to monosubstituted ortho or para bromo derivatives. We now report detailed studies of the effect of the structure of the polymeric reagent and the structure of the aromatic or heteroaromatic molecule on the course of bromination.

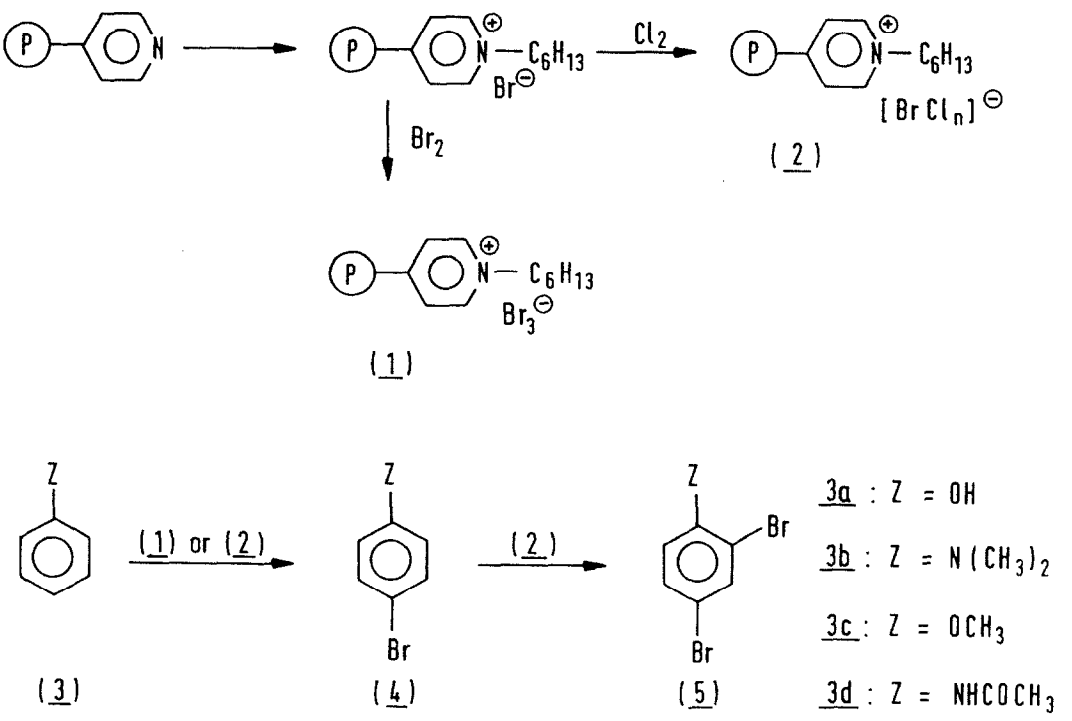
RESULTS AND DISCUSSION

Crosslinked polystyrene beads were usually used for the preparation of various immobilized reagents, while crosslinked copolymers with styrene and 4-vinylpyridine have received much less attention, in spite of a known fact that pyridine by itself or in conjunction with other reagents has a wide application in organic synthesis[12]. It has been already demonstrated that crosslinked co-poly/styrene-4-vinyl(N-methylpyridinium iodide)/ was transformed by chlorine to a reagent capable of chlorinating or iodinating various organic molecules[13].

Crosslinked co-poly/styrene-4-vinylpyridine/ was converted with 1-bromohexane to the pyridinium salt, which was further transformed by bromine or chlorine to reagent 1 (Scheme 1), containing 43.29%

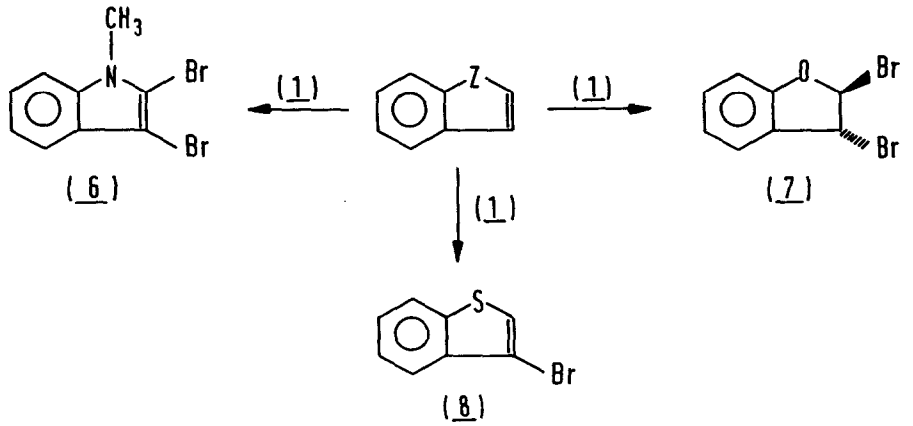
of bromine, or reagent 2, containing 10.8% of bromine and 30.1% of chlorine (independently we have found that the brominating capacity of 2 was 1.4 mmol per gram). Both reagents were first tested on the phenyl ring, bearing activating functional groups. Phenol (3a) rapidly reacted in a mixture of CH_2Cl_2 and CCl_4 (1:1) at room temperature with reagent 1 and after 2 hours, the crude reaction mixture contained only 4-bromophenol (4a), accompanied by 5% of 2,4-dibromophenol (5a), corresponding reaction with reagent 2 gave after 20 minutes 2,4-dibromophenol (5a) as the only product. The regiospecifity of phenol bromination strongly depended on the reagent used and the reaction conditions: 100% para regioselectivity was observed with N-bromosuccinimide in dimethylformamide[14], hexabromocyclopentadiene[15] and tetrabutylammonium dichlorobromate[16], while predominant ortho attack proceeded with N-bromosuccinimide in CCl_4 (86%) or with 2,4,4,6-tetrabromocyclohexa-2,5-dienone (87%)[17]. N,N-dimethylaniline was regiospecifically converted with 1 in methylene chloride at room temperature to the para isomer, and similar high regioselectivity was also observed with hexabromocyclopentadiene[14] or with a mixture of thallium(III)acetate and bromine[18], while reaction with potassium bromide in the presence of sulphuric acid proceeded predominantly to the ortho substituted derivative (64%)[19]. Methoxy (3c) and N-acetylaminobenzene (3d) were regiospecifically transformed in methanol at room temperature to para isomers, and similar regiospecifity was observed with other reagents[15,18,20]. According to the above findings, we further studied bromination of some reactive benzoheterocyclic compounds, i.e. N-methylindole, benzofuran, and benzo/b/thiophene with less reactive reagent 1 in methylene chloride at room temperature. In all three cases different types of products

SCHEME 1



were formed, i.e. 2,3-dibromo-N-methylindole (6), 2,3-dibromo-2,3-dihydrobenzofuran (7), and 3-bromobenzo/b/thiophene (8, Scheme 2) in yields over 90%, in contrast to the reactions with 2 which afforded complex reaction mixtures. N-acetyltyramine was converted with 2 in methanol to 3,5-dibromo-N-acetyltyramine (9) in 96% yield.

SCHEME 2



Steric interactions between organic molecules and polymer supported reagents are usually very important factors and in the case where greater steric hindrance appeared, the reaction failed, which prompted us to study the effect of alkyl group magnitude on the rate of bromination and on ortho/para regioselectivity in the benzene nucleus. The reactions of 2 with all the tested substrates, i.e. methyl, ethyl, iso-propyl, and tert-butylbenzene, were carried out under the same conditions (5-hours reaction at 85°C) in a mixture of acetic acid and water and the effect of alkyl group magnitude on the conversion and ortho-para regioselectivity is presented in Table 1. A larger alkyl group diminished the reactivity, but increased the para-ortho regioselectivity. Corresponding reactions with 1 resulted only in 1-2% conversion of the alkylbenzene. All four substrates have been studied several times with different reagents and again the important role of the reagent chosen was demonstrated[18,20-28].

TABLE 1

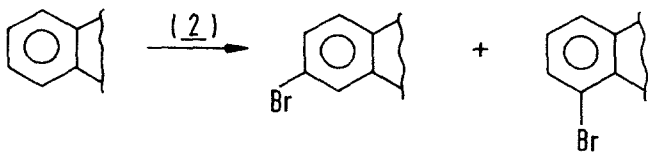
The Effect of Alkyl Group on Regioselectivity and Conversion of Benzene Derivatives with Polymer Supported Reagent 2

SUBSTRATE	CONVERSION[a] /%/	SUBSTITUTION	
		ortho	para
toluene	87	39	61
ethylbenzene	83	31	69
iso-propylbenzene	70	20	80
tert-butylbenzene	72	0	100

a/1 mmol of substrate; solvent: 85% (v/v) acetic acid (20 ml); reagent 2: 1.8 g; reaction temperature: 85°C; reaction time: 5 h

The influence of the attached alicyclic ring on the chemistry of benzocyclenes has received considerable attention from various points of view. Most of the work on indane and tetraline has been directed toward supporting or disproving the possibility first postulated in 1930 by Mills and Nixon[29] of bond fixation of these compounds. Examination of molecular models of o-xylene, indane, and tetraline shows that methylene groups adjacent to the aromatic ring in indane induce less steric hindrance in the α-position than methyl or methylene groups in o-xylene and tetraline[30]. Bromination of all three molecules hardly supported such an explanation, and for this reason, the transition state for α- and β-attack must be taken into account[31]. β-regiospecifity was even enhanced in comparison to bromination when fluorination with xenon difluoride was performed[32]. Brominations of o-disubstituted benzene derivatives were carried out at room temperature in a mixture of acetic acid and water in the dark with reagent 2. Crude reaction mixtures (90% yield) were analyzed by glc (reactions were also repeated according to the literature[31]) and the regiospecifity of bromination is presented in Scheme 3. It is evident that bromination with the polymer supported reagent has higher regioselectivity than reaction with bromine in acetic acid[30]; however a similar increase in the regiospecifity was also observed when bromination of o-xylene was performed in trifluoroacetic acid[22].

SCHEME 3



The Effect of Structure of o-Disubstituted Benzene Derivates on Regiospecifity of Bromination[a)]

	PRODUCT DISTRIBUTION			
	β-ATTACK [%]		α-ATTACK [%]	
SUBSTRATE	REAGENT (2)	Br_2[31]	REAGENT (2)	Br_2[31]
o-xylene	86	75	14	25
indane	93	84	7	16
tetraline	70	61	30	39

a/1 mmol of substrate; solvent: 85% (v/v) acetic acid (20 ml); reagent 2: 2.4 g; reaction temperature: 23°C; reaction time: 24 h.

In Table 2, the effect of the brominating reagent on regiospecifity in 1,2-dimethyl and 1,3-dimethylbenzene is presented. 1,4-dimethylbenzene was also converted with 2 to the monobromo derivative.

TABLE 2

The Effect of the Reagent on Bromination of 1,2- and 1,3-Dimethylbenzene

SUBSTRATE	REAGENT	PRODUCT DISTRIBUTION		ref.
		3-bromo	4-bromo	
1,2-dimethyl-benzene	$Br_2/FeCl_3$	67.1	32.9	23
	Br_2/CH_3COOH	25	75	31
	Br_2/CF_3COOH	12.5	87.5	27
	2[a]	14	86	
	$Br_2/Tl(OCOCH_3)_3$		100	18
		2-bromo	4-bromo	
1,3-dimethyl-benzene	$Br_2/FeCl_3$	21.2	79.8	23
	Br_2/CF_3COOH	3.7	96.3	27
	2[b]		100	
	$Br_2/Tl(OCOCH_3)_3$		100	18

a/1 mmol of substrate; solvent: 85% (v/v) acetic acid (20 ml); reagent 2: 2.4 g; reaction temperature: 23°C; reaction time: 24 h

b/1 mmol of substrate; solvent: methanol (20 ml); reagent 2: 1.2 g; reaction temperature: 23°C; reaction time: 24 h

EXPERIMENTAL SECTION

IR spectra were recorded with a Perkin Elmer 727 B spectrometer, ^1H nmr spectra with a Jeol JNM-PS-100 and Varian EM-360 instruments, with Me_4Si as internal reference. Mass spectra and high resolution measurements were taken on a CEC-21-110 spectrometer. Gas liquid partition chromatography was carried out on Varian Aerograph Models 2700 and 3700, and tlc on Merck PSC Fertigplatten silica gel or aluminium oxide F-254. Elemental analysis was carried out in the Pascher microanalytical laboratory, Bonn. Melting points were determined on a Kofler apparatus and are uncorrected. Poly/styrene-4-vinylpyridine/[5] (2% DVB), containing 42 - 44% of pyridine rings, was prepared according to the literature. Solvents were purified[33] before use.

Preparation of Polymeric Brominating Reagent 1 from Poly/Styrene-4-Vinylpyridine/

60 g of poly/styrene-4-vinylpyridine/ were suspended in 300 ml of methanol, stirred at room temperature (23°C) for three hours, and 6 mmols of n-hexylbromide per mmol of pyridine rings were slowly added. The reaction mixture was refluxed for 20 hours, the insoluble resin was filtered off, washed with methanol (twice) and chloroform (three times)(complete quarternization is reflected in the disappearance of the IR vibration at 1580 cm^{-1}, corresponding to $\nu C=N$ in the starting polymer) and suspended in 800 ml of chloroform. After swelling at 23°C for 24 hours, the suspension was cooled to 0°C and under stirring 44 g of bromine in 150 ml of chloroform was slowly added, stirred at 0°C for an additional 4 hours, the insoluble product filtered off, washed with chloroform, dried at room temperature for 20 hours and 115.5 g of polymeric product 1 was obtained. For elemental analysis, 1 was dried at 65°C for 4 hours and 43.29% of Br was determined.

Preparation of Polymeric Brominating Reagent 2 from Poly/Styrene-4-Vinylpyridine/

60 g of poly/styrene-4-vinylpyridine/ were suspended in 300 ml of methanol, stirred at room temperature (23°C) for three hours, and 6 mmols of n-hexylbromide per mmol of pyridine rings were slowly added. The reaction mixture was refluxed for 20 hours, the insoluble resin was filtered off, washed with methanol (twice) and chloroform (three times) and suspended in 800 ml of chloroform. After swelling for 24 hours at roomtemperature, the suspension was cooled to 0°C, and chlorine gas was introduced, until the yellow colour of the reaction mixture persisted after 30 minutes of stirring at room temperature. The reaction mixture was stirred for an additional 5 hours at 23°C, the insoluble product filtered off, washed with chloroform (three times) and after drying at room temperature for 20 hours, 119.5 g of polymeric product 2 were obtained. For elemental analysis, 2 was dried at 65°C for four hours, and 10.8% of bromine and 30.1% of chlorine were determined.

General Reaction Procedures

Procedure A

1 mmol of substrate was dissolved in 20 ml of 85% (v/v) acetic acid in water and the appropriate amount of polymeric reagent 2 was added. After a given time at a given temperature, the polymeric resin was filtered off, washed with methylene chloride, the reaction mixture was poured into water, extracted with methylene chloride, the methylene chloride layer washed with water, aqueous $NaHCO_3$, and water, and dried over anhydrous sodium sulphate. The solvent was evaporated in vacuo and the crude reaction mixture analyzed by glc and ^1H nmr. The reactions with o-xylene, indane, tetraline, and p-xylene, were carried out in the dark. The structures of the products were determined on the basis of the ir spectroscopic data and by comparison to the literature, or by comparison with theauthentic materials.

Procedure B

1 mmol of substrate was dissolved in 20 ml of the appropriate solvent and a given amount of polymeric reagent 1 or 2 was added. After a given time at a given temperature, the polymeric resins were filtered off, washed with solvent, the solvent evaporated in vacuo and the crude reaction mixtures analyzed by ^1H nmr and glc.

Bromination of Phenol (3a)

Procedure B: 2 g of polymeric reagent 1; solvent: methylene chloride : tetrachloromethane 1 : 1; 23°C; 2 hours; the product was isolated by preparative glc (OV 101 10%, Chromosorb W AW 60/80, 145°C) and 118 mg (68%) of crystalline *4-bromophenol*[34] (4a), mp = 62 - 63°C (mp_{lit}[34] = 64 - 65°C), was obtained.

Procedure B: 2.4 g of 2; solvent: methylene chloride : tetrachloromethane 1 : 1; 23°C; 20 minutes; the product was isolated by preparative glc (OV 101 10%, Chromosorb W AW 60/80, 175°C) and 194 mg (77%) of crystalline *2,4-dibromophenol*[35] (5a), mp = 37 - 38°C (mp_{lit}[35] = 40°C), was obtained.

Bromination of N,N-Dimethylaniline (3b)

Procedure B: 1.2 g of 1; solvent: methylene chloride; 23°C; 20 minutes; the crude product was crystallized from tetrachloromethane and 147 mg (73.5%) of crystalline *4-bromo-N,N-dimethylaniline*[36] (4b), mp = 54 - 54.5°C (mp_{lit}[36] = 55°C) was obtained.

Bromination of Methoxybenzene (3c)

Procedure B: 1.2 g of 2; solvent: methanol; 23°C; 20 minutes; the product was isolated by preparative glc (FFAP 30%, Chromosorb W AW 100/120, 150°C), and 144.5 mg (77%) of oily *4-bromomethoxybenzene*[37] (4c), was obtained.

Bromination of N-Acetylaminobenzene (3d)

Procedure B: 1.2 g of 2; solvent: methanol; 23°C; 20 minutes; the crude product was crystallized from acetone and 152 mg (71%) of crystalline *1-N-acetylamino-4-bromobenzene*[36] (4d), mp = 169 - 170°C (mp_{lit}[36] = 165°C), was obtained.

Bromination of 1-Methylindole

Procedure B: 1.2 g of 1; solvent: methylene chloride; 23°C; 20 minutes; the product was isolated by preparative tlc (SiO_2, methylene chloride : petroleum ether 1.5 : 8.5) and 208 mg (72%) of crystalline *2,3-dibromo-1-N-methylindole* (6), mp = 39 - 40°C, was obtained: ^1H nmr ($CDCl_3$): 3.66 ppm (s, 3H), 7.13 ppm (m, 3H), 7.47 ppm (m, 1H); mass spectrum calcd. for $C_9H_7NBr_2$ m/z 286.8946, found m/z 286.8949, m/z: 292 (M^+ + 5, 5%), 291 (M^+ + 4, 50), 290 (M^+ + 3, 16), 289 (M^+ + 2, 100), 288 (M^+ + 1, 16), 287 (M^+, 51), 274 (15), 169 (12), 167 (12), 129 (16), 128 (13), 114 (33), 102 (11), 88 (18), 87 (11), 62 (14).

Bromination of Benzo/b/thiophene

Procedure B: 2.4 g of 1; solvent: methylene chloride; 23°C; 22 hours; the product was isolated by preparative tlc (SiO_2, petroleum ether) and 168 mg (78.5%) of oily *3-bromo-benzo/b/thiophene*[38] (8) was obtained.

Bromination of Benzofuran

Procedure B: 1.6 g of 1; solvent: methylene chloride; 23°C; 3 hours; crystallization of the crude product from petroleum ether gave 212 mg (76%) of crystalline *trans-2,3-dibromo-2,3-dihydrobenzofuran*[39] (7), mp = 85.5 - 86.5°C (mp_{lit}[39] = 86°C).

Bromination of N-Acetyltyramine

Procedure B: 2.4 g of 2; solvent: methanol; 23°C; 1 hour; the crude product was crystallized from a mixture of methylene chloride and methanol and 270.4 mg (84%) of crystalline *3,5-dibromo-N-acetyltyramine* (9), mp = 142.5 - 143.5°C, was obtained: ^1H nmr ($(CD_3)_2CO$): 2.77 ppm (t, J = 6.5 Hz, 2H), 3.48 ppm (t, J = 6.5 Hz, 2H), 7.26 ppm (s, 2H); mass spectrum: calcd. for $C_{10}H_{11}NO_2Br_2$ m/z 334.9158, found m/z 334.9155, m/z: 339 (M^+ + 4, 2.5%), 337 (M^+ + 2, 5), 335 (M^+, 2.5), 280 (26), 278 (52), 276 (27), 200 (23), 198 (25), 77 (17), 76 (12), 75 (13), 72 (27), 60 (27), 53 (10), 51 (22), 50 (11), 43 (100).

Bromination of o-Xylene

Procedure A: 2.4 g of 2; 23°C; 24 hours; the crude reaction mixture was analyzed by glc (DNP 30% 3 m, Chromosorb W AW 100/120, T = 120°C) and separated by preparative glc: 17 mg (9.2%) of *3-bromo*[31] and 105 mg (63.5%) of *4-bromo-o-xylene*[31] was isolated.

Bromination of Indane

Procedure A: 2.4 g of 2; 23°C; 24 hours; the crude reaction mixture was analyzed by glc (DNP 10% 3 m, Chromosorb W HP 80/100, 140°C) and separated by preparative glc: 13.0 mg (6.6%) of *α-bromoindane*[31] and 116 mg (59%) of *β-bromoindane*[31] were isolated.

Bromination of Tetraline

Procedure A: 2.4 g of 2; 23°C; 24 hours; the crude reaction mixture was analyzed by glc (DNP 15% 2 m, Chromosorb W AW 100/120, 155°C) and separated by preparative glc: 12 mg (5.7%) of *α-bromotetraline*[31] and 112 mg (48.4%) of *β-bromotetraline*[31] were isolated.

Bromination of Toluene

Procedure A: 1.8 g of 2; 85°C; 5 hours; the crude reaction mixture was analyzed by glc (DNP 15% 3 m, Chromosorb W AW 100/120, 100°C) and separated by preparative glc: 47.6 mg (28%) of *2-bromotoluene*[22] and 73.4 mg (43%) of *4-bromotoluene*[22] were isolated.

Bromination of Ethylbenzene

Procedure A: 1.8 g of 2; 85°C; 5 hours; the crude reaction mixture was analyzed by glc (DNP 15% 3 m, Chromosorb W AW 100/120, 130°C) and separated by preparative glc: 32 mg (17.4%) of *2-bromoethylbenzene*[22] and 73.8 mg (40%) of *4-bromoethylbenzene*[22] were isolated.

Bromination of iso-Propylbenzene

Procedure A: 1.8 g of 2; 85°C; 5 hours; the crude reaction mixture was analyzed by glc (FFAP 30%, Chromosorb W AW 100/120, 105°C) and separated by preparative glc: 20.8 mg (10.5%) of *2-bromo-iso-propylbenzene*[22] and 79.2 mg (40%) of *4-bromo-iso-propylbenzene*[22] were isolated.

Bromination of tert-Butylbenzene

Procedure A: 1.8 g of 2; 85°C; 5 hours; the crude reaction mixture was analyzed by glc (FFAP 30%, Chromosorb W AW 100/120, 105°C) and 126 mg (59%) of *4-bromo-tert-butylbenzene*[21] was isolated by preparative glc.

Bromination of 1,3-Dimethylbenzene

Procedure B: 1.2 g of 2; solvent: methanol; 23°C; 24 hours; the product was isolated by preparative glc (FFAP 30%, Chromosorb W AW 100/120, 185°C) and 132 mg (72%) of *4-bromo-1,3-dimethylbenzene*[11,18,27] was obtained.

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