The conditions used for the preparation of alkyl halides from alcohols were identical with or similar to those illustrated in the preparation of benzyl chloride. The yields, reaction temperature, times are compiled in Table I. Most alkyl chlorides were fractionally distilled by using a 20-cm Vigreux column. 1-Hexyl chloride, 2-hexyl chloride, cyclohexyl chloride, 2-methyl-3-buten-2-ol, and neopentyl chloride were distilled by using a spinning-band still. The identity of the alkyl chloride was confirmed by comparing proton NMR data[17] and gas chromatographic retention times with those of authentic samples.

Chlorination with Dichlorodimethylsilane. Selenium dioxide (0.18 g) was added to 13.5 g of dichlorodimethylsilane (105 mmol) in 10 mL of carbon tetrachloride, and the mixture was stirred until it became homogeneous. *tert*-Butyl alcohol (7.4 g, 100 mmol) was slowly added. After standing for 2 h at 20 °C, the mixture was slowly distilled through a fractionating column to obtain 8.6 g (93%) of 2-chloro-2-methylpropane, bp 51–52 °C. Following the same procedure, benzyl chloride was prepared in 95% yield.

Acknowledgment. Financial support from the Korea Science and Engineering Foundation is gratefully acknowledged.

Registry No. Chlorotrimethylsilane, 75-77-4; selenium dioxide, 7446-08-4; benzyl alcohol, 100-51-6; 4-methoxybenzyl alcohol, 105-13-5; 2-naphthylmethanol, 1592-38-7; cyclohexylmethanol, 100-49-2; neopentyl alcohol, 75-84-3; 1-hexanol, 111-27-3; 2-hexanol, 626-93-7; cyclohexanol, 108-93-0; 4-*tert*-butylcyclohexanol, 98-52-2; menthol, 89-78-1; *tert*-butyl alcohol, 75-65-0; 1,1-diphenylethanol, 599-67-7; (*E*)-cinnamyl alcohol, 4407-36-7; 2-methyl-3-buten-2-ol, 115-18-4; geraniol, 106-24-1; borneol, 507-70-0; ethylene glycol, 107-21-1; 1,4-butanediol, 110-63-4; benzyl chloride, 100-44-7; 4-methoxybenzyl chloride, 824-94-2; 2-naphthylmethyl chloride, 2506-41-4; cyclohexylmethyl chloride, 1072-95-3; neopentyl chloride, 753-89-9; 1-chlorohexane, 544-10-5; 2-chlorohexane, 638-28-8; chlorocyclohexane, 542-18-7; 4-*tert*-butylcyclohexyl chloride, 62056-46-6; menthyl chloride, 16052-42-9; *tert*-butyl chloride, 507-20-0; (*E*)-cinnamyl chloride, 21087-29-6; 3-methyl-2-butenyl chloride, 503-60-6; linalyl chloride, 471-10-3; bornyl chloride, 464-41-5; selenium(IV) oxychloride, 7791-23-3; 1,1-diphenylethyl chloride, 947-40-0; 1,1-diphenylethylene, 530-48-3; geranyl chloride, 5389-87-7; dichlorodimethylsilane, 75-78-5.

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Synthesis of (2,2,2-Trifluoroethyl)benzene Derivatives[1]

Akira Ando, Takuichi Miki, and Itsumaro Kumadaki*

Faculty of Pharmaceutical Sciences, Setsunan University, 45-1, Nagaotoge-cho, Hirakata, Osaka 573-01, Japan

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Introduction

Organic fluorine compounds containing a trifluoromethyl group have lately attracted considerable attention because of their biological activities.[2] In previous papers, we reported the trifluoromethylation[3] of aromatic halides with trifluoromethyl copper and the trifluoropropylation[4] of aromatic compounds by the Friedel–Crafts reaction of trifluoropropene in the presence of HBF_4 as a catalyst. In the former, the trifluoromethyl group was directly attached to an aromatic ring, while in the latter, it was linked by a two-methylene bridge to an aromatic ring. Aromatic trifluoromethyl compounds were widely used as medicines or agricultural chemicals.[2] Trifluoropropyl compounds showed interesting physicochemical and physiological properties, also.[5] Therefore, we were interested in the property of trifluoroethyl compounds, since a trifluoroethyl group is located between the lower (CF_3) and the higher ($CH_2CH_2CF_3$) analogues and also represents a CF_3 group connected to the aromatic ring by a methylene bridge. Although various methods for the synthesis of trifluoroethyl compounds have been reported,[6] they have disadvantages such as use of a highly toxic reagent, low yields, and/or multistep procedures. No convenient routes to trifluoroethyl compounds were available. Now, we report the synthesis of trifluoroethyl compounds from aromatic amines by trichloroethylation followed by the Cl to F halogen exchange reaction of the trichloroethyl derivatives.

Scheme I

$$\underset{1}{ArNH_2} + CH_2{=}CCl_2 \xrightarrow[CuCl_2\text{-}CH_3CN]{t\text{-}BuONO} \underset{2}{ArCH_2CCl_3}$$

Scheme II

$$\underset{2a}{p\text{-}NO_2C_6H_4CH_2CCl_3} \xrightarrow[DMF]{KF} \text{decomposed}$$

$$\mathbf{2a} \xrightarrow{HF} \underset{4a}{p\text{-}NO_2C_6H_4CH_2CF_2Cl} + \underset{5}{p\text{-}NO_2C_6H_4CH_2COOH}$$

Scheme III

$$\underset{2a\text{-}d}{ArCH_2Cl_3} \xrightarrow{SbF_3\text{-}SbCl_5} \underset{3}{ArCH_2CF_3} + \underset{4}{ArCH_2CF_2Cl} + \underset{6}{ArCHClCF_2Cl} + \underset{7}{ArCH{=}CCl_2} + \underset{8}{ArCCl{=}CCl_2}$$

Table I. Trichloroethylation of Aromatic Amines 1

Ar	yield of 2 (%)	Ar	yield of 2 (%)
a 4-NO_2Ph	64	**d** 4-CH_3Ph	57
b 3-NO_2Ph	71	**e** 3-ClPh	65
c 3-CF_3Ph	73	**f** 4-ClPh	61

Discussion

Trichloroethyl derivatives were reported to have been prepared by the Meerwein arylation of aromatic amines.[7] However, a straight application of the general procedure of this reaction gave low yields of trichloroethyl compounds **2**. Doyle and his co-workers reported the similar reaction of acrylonitrile.[8] They treated aromatic amines with *tert*-butyl nitrite followed by the reaction with acrylonitrile in acetonitrile. We applied this modified procedure to 1,1-dichloroethylene (Scheme I) and isolated in fairly good yield compound **2**, irrespective of the electronic properties of the substituents on the starting arylamines. The results are shown in Table I.

Next, we attempted to convert the trichloroethyl group into a trifluoroethyl group.[9] When the *p*-nitro trichloro compound **2a** was heated with potassium fluoride in di-

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(8) Doyle, M. P.; Siegfried, B.; Elliott, R. C.; Dellaria, J. F., Jr. *J. Org. Chem.* **1977**, *42*, 2431.
(9) For the replacement of chlorine atoms with fluorine atoms, several methods were reported. See: *Chemistry of Organic Fluorine Compounds*; Hudlicky, M., Ed., Ellis Horwood Ltd.; Chichester, 1976.

0022-3263/88/1953-3637$01.50/0

Table II. Fluorination of Trichloroethyl Compounds 2

entry	Ar	2/SbF_3/$SbCl_5$	conditions	3, yield (%)
2a	4-NO_2Ph	1:4.5:1.5	65 °C, 1 h	41[a]
2b	3-NO_2Ph	1:3.5:0.4	50 °C, 0.6 h	trace[b]
		1:3.6:1.2	65 °C, 1 H	48[c]
		1:5.3:1.8	65 °C, 1 h	36[d]
		1:3.5:2.4	65 °C, 4 h	34[e]
2c	3-CF_3Ph	1:3.9:1.4	60 °C, 0.5 h	34[f]
2d	4-CH_3Ph	1:3.0:1.1	80 °C, 0.1 h	trace[g]
2c	3-CF_3Ph	1:5.1:1.7	CH_2Cl_2, 0.5 h	51[h]
2d	4-CH_3Ph	1:4.5:1.5	CH_2Cl_2, 4.3 h	12[i]

[a] Other products: dichlorodifluoroethyl compound (**6a**, 7%), dichloroethylene compound (**7a**, 17%), trichloroethylene compound (**8a**, 29%). [b] Major product: dichloroethylene compound (**7b**, 74%). **3b** and **4b** were detected by ^{19}F NMR and GLC–mass spectra. [c] Byproducts: dichlorodifluoroethyl compound (**6b**, 10%), trichloroethylene compound (**8b**, 33%). [d] Other products: dichlorodifluoroethyl compound (**6b**, 17%), trichloroethylene compound (**8b**, 40%). [e] Other products: dichlorodifluoroethyl compound (**6b**, 3%), trichloroethylene compound (**8b**, 30%), dichlorotrifluoro compound (19%). [f] Byproducts: 3-trifluoroethylbenzoic acid (17%), dichlorodifluoroethyl compound (**6c**, 17%). [g] Major part was tarry substances. **3d** and **4d** were detected by ^{19}F NMR and GLC–mass spectra. [h] Other products: 3-trifluoroethylbenzoic acid (6%), dichlorodifluoroethyl compound (**6c**, 13%). [i] Other product: chlorodifluoroethyl compound (**4d**, 3%).

methylformamide, only the decomposition of **2a** was observed. Treatment of **2a** with anhydrous hydrogen fluoride gave a small amount chlorodifluoroethyl compound **4a** (9%) with *p*-nitrophenylacetic acid (**5**, 64%) as a major product. Formation of **5** may be attributed to a small amount of water in the hydrogen fluoride. (Scheme II).

As hydrogen fluoride was found not to be reactive enough for the complete fluorination, antimony trifluoride was examined as the fluorinating agent. Although it is well known that antimony trifluoride is used as a fluorinating agent of benzotrichloride derivatives,[10] treatment of **2a** with this reagent resulted in the recovery of the starting material.

Next, we examined the reaction with antimony trifluoride in the presence of antimony pentachloride. Both reagents were mixed under stirring, compound **2b** was added, and the mixture was stirred at 60–65 °C (see Scheme III). Some reactions are summarized in Table II. Yields of the desired products were affected by the amount of antimony pentachloride and the reaction time. For example, when approximately 1 mol of antimony pentachloride and 3 mol of antimony trifluoride were used, **3b** was obtained in 48% yield. If only a small amount of antimony pentachloride was used, the yield of **3b** was very low, and the dehydrochlorination reaction occurred preferentially. The byproducts originated from the chlorination of α-position, probably due to the oxidative property of antimony pentachloride. The *p*-nitro compound gave a comparable yield of the trifluoroethyl compound to that obtained from the meta isomer. In the case of **2a**, a considerable amount of vinyl compounds was obtained. This may be attributed to the high reactivity of benzylic hydrogen due to the electron-attracting effect of the *p*-nitro group. In the case of a *m*-trifluoromethyl compound (**2c**), hydrolysis of the trifluoromethyl group became evident, by the formation of the benzoic acid (see footnote f, Table II).

The reaction of a *p*-methyl compound (**2d**) was rather messy, and only traces of **3d** and the chlorodifluoroethyl compound were detected by ^{19}F NMR and GLC–mass spectrum. This may be due to the high reactivity of the benzene ring compared with the corresponding nitro- or trifluoromethyl-substituted counterparts. Methylene chloride was used as a solvent to avoid this polymerization. In this case, an improvement of the yield of **3d** was observed. This fact suggests that the high dilution method may improve the yield of this reaction.

(10) (a) Swarts, F. *Bull. Acad. R. Belg.* **1920**, 389. (b) Henne, A. L. *Org. React. (N.Y.)* **1944**, *2*, 49.

Experimental Section

A typical experimental procedure is as follows: To antimony trifluoride (2.04 g, 11.4 mmol), dried and powdered under vacuum, was added antimony pentachloride (0.5 mL, 3.9 mmol) dropwise via syringe at 0 °C under an argon atmosphere. After stirring was continued for 15 min at room temperature, the mixture was heated at 65 °C for 15 min. At this temperature, 1,1,1-trichloro-2-(*m*-nitrophenyl)ethane (**2b**, 811 mg, 3.19 mmol) was added to the mixture in several portions. After stirring for 1 h, water and ether were added to the reaction mixture. The resulting suspension was filtered through a Celite layer and extracted with ether. The combined etherial layer was washed with 20% HCl and water and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography (SiO_2–hexane). The first fraction gave (*m*-nitrophenyl)trichloroethylene (**8b**, 267.5 mg, 33%). The second fraction gave 1,2-dichloro-2,2-difluoro-1-(*m*-nitrophenyl)ethane (**6b**, 80.8 mg, 10%). The third fraction gave 1,1,1-trifluoro-2-(*m*-nitrophenyl)ethane (**3b**, 316.1 mg, 48%).

Other physicochemical data of the products are as follows. **4a**: light yellow crystals, mp 48.5–49.5 °C; mass spectrum, *m/z* 221 (M^+); high resolution mass spectrum, calcd for $C_8H_6NO_2F_2Cl$ 221.0055, found 221.0065; IR (KBr) cm^{-1} 1530, 1355 (NO_2), 1180, 1110 (C–F); ^1H NMR ($CDCl_3$) δ 8.19 (2 H, d, J = 9 Hz), 7.46 (2 H, d, J = 9 Hz), 3.67 (2 H, t, J_{H-F} = 12.2 Hz); ^{19}F NMR ($CDCl_3$, ppm from $PhCF_3$) −11.58 (2 F, t, J_{H-F} = 12.2 Hz).

5: yellow crystals, mp 151–152 °C; mass spectrum, *m/z* 181 (M^+); high resolution mass spectrum, calcd for $C_8H_7NO_4$ 181.0375, found 181.0374; IR (KBr) cm^{-1} 1696 (COOH), 1350 (NO_2); ^1H NMR ($CDCl_3$) δ 8.13 (2 H, d, J = 8 Hz), 7.41 (2 H, d, J = 8 Hz), 3.75 (2 H, s).

3a: colorless crystals, mp 65.5–66.5 °C; mass spectrum, *m/z* 205 (M^+); high resolution mass spectrum, calcd for $C_8H_6NO_2F_3$ 205.0350, found 205.0350; IR (KBr) cm^{-1} 1530, 1360 (NO_2), 1264, 1154 (C–F); ^1H NMR ($CDCl_3$) δ 8.20 (2 H, d, J = 9 Hz), 7.46 (2 H, d, J = 9 Hz), 3.5 (2 H, q, J_{H-F} = 10.5 Hz); ^{19}F NMR ($CDCl_3$, ppm from $PhCF_3$) 2.72 (3 F, t, J_{H-F} = 10.5 Hz).

6a: yellow oil; mass spectrum, *m/z* 255 (M^+); high resolution mass spectrum, calcd for $C_8H_5NO_2F_2Cl_2$ 254.9666, found 254.9668; IR (KBr) cm^{-1} 1530, 1350 (NO_2), 1120, 1110 (C–F); ^1H NMR ($CDCl_3$) δ 8.24 (2 H, d, J = 9 Hz), 7.68 (2 H, d, J = 9 Hz), 5.3 (1 H, dd, J_{H-F} = 7.5 Hz, $J_{H-F'}$ = 9.5 Hz); ^{19}F NMR ($CDCl_3$, ppm from $PhCF_3$) −4.76 (1 F, dd, J_{H-F} = 7.5 Hz, $J_{F-F'}$ = 164.8 Hz), −2.03 (1 F, dd, $J_{H-F'}$ = 9.5 Hz, $J_{F-F'}$ = 164.8 Hz).

7a: light yellow crystals, mp 88.5–89.5 °C; mass spectrum, *m/z* 217 (M^+); high resolution mass spectrum, calcd for $C_8H_5NO_2Cl_2$ 216.9698, found 216.9704; IR (KBr) cm^{-1} 1520, 1340 (NO_2); ^1H NMR ($CDCl_3$) δ 8.2 (2 H, d, J = 9 Hz), 7.7 (2 H, d, J = 9 Hz), 6.9 (1 H, s).

8a: colorless crystals, mp 52–53 °C; mass spectrum, *m/z* 251 (M^+); high resolution mass spectrum, calcd for $C_8H_4NO_2Cl_3$ 250.9307, found 250.9301; IR (KBr) cm^{-1} 1516, 1358 (NO_2); ^1H NMR ($CDCl_3$) 7.65 (2 H, d, J = 9 Hz), 8.23 (2 H, d, J = 9 Hz).

3b: light yellow crystals, mp 42–43 °C; mass spectrum, *m/z* 205 (M^+); high resolution mass spectrum, calcd for $C_8H_6NO_2F_3$ 205.0350, found 205.0343; IR (KBr) cm^{-1} 1540, 1370 (NO_2), 1270, 1150 (C–F); ^1H NMR ($CDCl_3$) δ 8.15 (2 H, m), 7.6 (2 H, m), 3.49 (2 H, q, J_{H-F} = 10.3 Hz); ^{19}F NMR ($CDCl_3$, ppm from $PhCF_3$) 3.07 (3 F, t, J_{H-F} = 10.3 Hz).

6b: yellow crystals, mp 46–47 °C; mass spectrum, *m/z* 255 (M^+); high resolution mass spectrum, calcd for $C_8H_5NO_2F_2Cl_2$ 254.9666, found 254.9671; IR (KBr) cm^{-1} 1540, 1355 (NO_2), 1195, 1120 (C–F); ^1H NMR ($CDCl_3$) δ 8.38 (1 H, m), 8.33 (1 H, m), 7.89 (1 H, J = 7.9 Hz), 7.63 (1 H, dd, $J = J'$ = 7.9 Hz), 5.34 (1 H, dd, J_{H-F} = 9.8 Hz, $J_{H-F'}$ = 7.3 Hz); ^{19}F NMR ($CDCl_3$, ppm from $PhCF_3$) −4.53 (1 F, dd, $J_{H-F'}$ = 7.3 Hz, $J_{F-F'}$ = 163.6 Hz), −1.80 (1 F, dd, J_{H-F} = 9.8 Hz, $J_{F-F'}$ = 163.6 Hz).

7b: light yellow crystals, mp 50–50.5 °C; mass spectrum, *m/z*

217 (M^+); high resolution mass spectrum, calcd for $C_8H_5NO_2Cl_2$ 216.9697, found 216.9697; IR (CCl_4) cm^{-1} 1620 (C=C), 1540, 1360 (NO_2); ^1H NMR ($CDCl_3$) δ 8.4 (1 H, m), 8.17 (1 H, ddd, J = 7.9 Hz, 2.2 Hz, 1.32 Hz), 7.84 (1 H, m, J = 7.9 Hz, J' = 1.32 Hz), 7.56 (1 H, dd, $J = J'$ = 7.9 Hz), 6.93 (1 H, s).

8b: colorless crystals, mp 62.5-63 °C; mass spectrum, m/z 251 (M^+); high resolution mass spectrum, calcd for $C_8H_4NO_2Cl_3$ 250.9308, found 250.9308; IR (KBr) cm^{-1} 1540, 1350 (NO_2); ^1H NMR ($CDCl_3$) δ 8.38 (1 H, m), 8.26 (1 H, ddd, J = 7.9 Hz, 2.1 Hz, 1.54 Hz), 7.84 (1 H, ddd, J = 7.9 Hz, 1.54 Hz, 1.54 Hz), 7.61 (1 H, ddd, J = 7.9 Hz, 7.9 Hz, 0.66 Hz).

3c: colorless oil; mass spectrum, m/z 228 (M^+); high resolution mass spectrum, calcd for $C_9H_6F_6$ 228.0374, found 228.0377; IR (neat) cm^{-1} 1334, 1260, 1136, 1078 (C-F); ^1H NMR ($CDCl_3$) δ 7.47 (4 H, m), 3.38 (2 H, q, J_{H-F} = 10.5 Hz); ^{19}F NMR ($CDCl_3$, ppm from $PhCF_3$) 0 (3 F, s), 3.16 (3 F, t, J = 10.5 Hz).

6c: colorless oil; mass spectrum, m/z 278 (M^+); high resolution mass spectrum, calcd for $C_9H_5F_5Cl_2$ 277.9688, found 277.9679; IR (neat) cm^{-1} 1336, 1174, 1140 (C-F); ^1H NMR ($CDCl_3$) δ 7.67 (4 H, m), 5.25 (1 H, dd, J_{H-F} = 7.3 Hz, $J_{H-F'}$ = 9.8 Hz); ^{19}F NMR ($CDCl_3$) -4.68 (1 F, dd, $J_{F-F'}$ = 163.58 Hz, J_{H-F} = 7.3 Hz), -1.90 (1 F, dd, $J_{F-F'}$ = 163.58 Hz, J_{H-F} = 9.8 Hz), 0.06 (3 F, s).

3d: colorless crystals, mp 44-45 °C; mass spectrum, m/z 174 (M^+); high resolution mass spectrum, calcd for $C_9H_9F_3$ 174.0657, found: 174.0658; IR (CCl_4) cm^{-1} 1262, 1138 (C-F); ^1H NMR ($CDCl_3$) δ 7.13 (4 H), 3.3 (2 H, q, J_{H-F} = 10.75 Hz), 2.33 (3 H, s); ^{19}F NMR ($CDCl_3$, ppm from $PhCF_3$) 3.37 (3 F, t, J_{H-F} = 10.75 Hz).

4d: colorless oil; mass spectrum, m/z 190 (M^+); high resolution mass spectrum, calcd for $C_9H_9F_2Cl$ 190.0360, found 190.0360; IR (neat) cm^{-1} 1260, 1088 (C-F); ^1H NMR ($CDCl_3$) δ 7.18 (4 H, s), 3.52 (2 H, J_{H-F} = 13.4 Hz), 2.35 (3 H, s); ^{19}F NMR ($CDCl_3$, ppm from $PhCF_3$) -11.5 (2 F, t, J_{H-F} = 13.4 Hz).

3-(Trifluoroethyl)benzoic acid: colorless crystals, mp 115-118 °C; mass spectrum, m/z 204 (M^+); high resolution mass spectrum, calcd for $C_9H_7O_2F_3$ 204.0368, found 204.0397; IR (KBr) cm^{-1} 1630 (COOH), 1258, 1158 (C-F); ^1H NMR ($CDCl_3$) δ 9.37 (1 H, b), 8.07 (m, 2 H), 7.56 (m, 2 H), 3.46 (2 H, q, J_{H-F} = 10.6 Hz); ^{19}F NMR ($CDCl_3$, ppm from $PhCF_3$) 3.16 (3 F, t, J_{H-F} = 10.6 Hz).

Conclusion

As described above, the present method offers a new process for the synthesis of trifluoroethyl compounds from aromatic amines. We are now searching a new catalyst which does not cause the benzylic halogenation and the polymerization of benzene derivatives substituted with electron-donating groups.

Registry No. **1a**, 100-01-6; **1b**, 99-09-2; **1c**, 98-16-8; **1d**, 106-49-0; **1e**, 108-42-9; **1f**, 106-47-8; **2a**, 2201-11-8; **2b**, 89894-59-7; **2c**, 30359-53-6; **2d**, 2201-10-7; **2e**, 114980-29-9; **2f**, 3883-14-5; **3a**, 3764-36-1; **3b**, 114980-30-2; **3c**, 50562-22-6; **3d**, 50562-01-1; **4a**, 114980-31-3; **4d**, 114980-32-4; **5**, 104-03-0; **6a**, 114980-33-5; **6b**, 114980-34-6; **6c**, 114980-35-7; **7a**, 5281-22-1; **7b**, 65085-93-0; **8a**, 4714-36-7; **8b**, 713-33-7; CH_2=CCl_2, 75-35-4; 3-(trifluoroethyl)benzoic acid, 114980-36-8.

A Novel Approach to the Synthesis of Two Versatile Synthetic Intermediates, 2,3-Bis(bromomethyl)-1,3-butadiene and Tetrakis(bromomethyl)ethylene

Syed Mashhood Ali, Shigeo Tanimoto,* and Tadashi Okamoto

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

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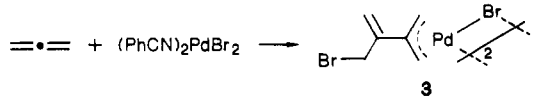
2,3-Bis(bromomethyl)-1,3-butadiene (**1**) is a versatile reactive synthetic intermediate that can be reacted under variety of conditions as a highly reactive 1,4-bis(allyl) dibromide in displacement reactions or as a 1,3-diene in Diels-Alder and cheletropic additions. The synthetic versatility of **1** has already been demonstrated through consecutive use of its allylic dibromide and conjugated diene functions with eventual further modification of the products.[1-6] Moreover, the primary products thus obtained constitute in themselves other new reactive intermediates since they conserve the feature of either a 1,3-diene or a 1,4-dibromo 2-ene derivatives. Besides, the dibromide **1** serves as a direct or indirect precursor[4,5] to the 2,2'-diallyl radical,[6] which is of topical interest in discussing the limits of Hund's rule.[7]

The dibromide **1** is generally obtained by the metal-induced debromination of tetrakis(bromomethyl)ethylene (**2**) in a variety of solvents,[3a,8] the best results being reported in ether with added HMPT.[1] However, the product is contaminated by the undesired polymeric products. The preparation of **1** from 3,4-bis(bromomethyl)-2,5-dihydrothiophene 1,1-oxide by the thermal elimination of SO_2 has also been reported in 31% yield.[3b] The tetrabromide **2**, immediate precursor of **1**, is generally prepared from 2,3-dimethyl-1,3-butadiene by the bromination with bromine and *N*-bromosuccinimide in 60% yield.[9] The preparation of **2** from the hexane or hexene isomers possessing the same carbon skeleton[10] and from pinacolyl alcohol[11] has been reported in 35% and 43% yields, respectively. In this note, we report a very simple, most efficient, and high yield synthesis of 2,3-bis(bromomethyl)-1,3-butadiene (**1**) and tetrakis(bromomethyl)ethylene (**2**) by the reaction of (π-allyl)palladium complex (**3**) with bromine and iodine monobromide, separately.

1 **2**

In the course of our investigations directed toward the synthesis of biologically significant polycyclic compounds, we have been inspired to investigate the reaction of (π-allyl)palladium complex (**3**) with bromine and iodine monobromide in pursuit of a highly attractive strategy for the preparation of 2,3-bis(bromomethyl)-1,3-butadiene (**1**) at the intermediate level. Our strategy was based on the oxidative cleavage of the complex **3** aimed at the regeneration of palladium(II) bromide used in the preparation of **3** (eq 1). (π-Allyl)palladium complex (**3**) is produced



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