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

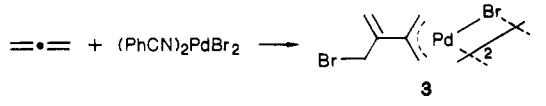

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Table I. Reaction of (π-Allyl)palladium Complex (3) with Bromine and Iodine Monobromide[a]

run	reagnt	subst/reagnt molar ratio	time (h)	yield[b] (%)	product (selectivity)
1	Br_2	1:1	0.5	88[c]	1
2	Br_2	1:2	0.5	92	1
3	Br_2	1:3	2.0	90	1 (54) + 2 (46)[d]
4	Br_2	1:4	2.0	98	2
5	IBr	1:1	0.5	85[c]	1
6	IBr	1:2	0.5	89	1
7	IBr	1:3	2.0	95	1 (58) + 2 (42)[d]
8	IBr	1:4	3.0	94	2[e]
9	IBr	1:8	2.0	97	2[f]

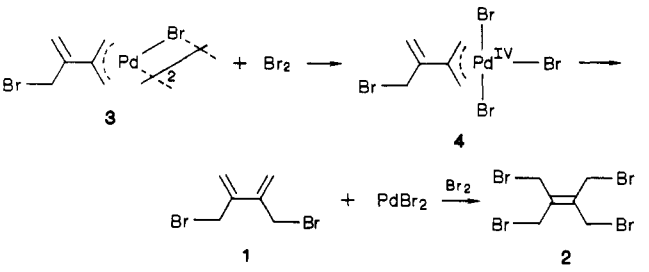
[a] Reaction conditions, see Experimental Section. The reactions were carried out on a 100-mg scale. [b] Based on the isolated product/s. [c] Calculated on the basis of complex recovered unreacted. [d] Determined by the ^1H NMR and GC–MS data. [e] Although the GC–MS confirmed it to be 2, the ^1H NMR spectrum displayed a broad split singlet instead of a sharp singlet as in other cases. [f] The use of excess amount of IBr is recommended for the preparation of 2.

in high yield by the reaction of allene, a cheap commodity obtained by the pyrolysis of hydrocarbons, with bis(benzonitrile)palladium(II) bromide in benzonitrile.[12] The oxidative cleavage of 3, produced in situ, with copper(II) bromide to give the dibromide 1 in 32% yield, based on the allene, has recently been reported.[13] The results are summarized in Table I.

The reaction of (π-allyl)palladium complex (3) with 2 molar equiv of bromine furnished 2,3-bis(bromomethyl)-1,3-butadiene (1) in 92% yield. In the run with 1 molar equiv of bromine, although 1 was the only product, the conversion was almost 50%, suggesting that 2 molar equiv of bromine are required for the conversion of 1 molar equiv of 3 to 1. However, when the reaction was conducted in the 1:4 molar ratio of complex to bromine, no dibromide 1 was formed and the product obtained after usual workup of the reaction was found to be tetrakis(bromomethyl)-ethylene (2). The reaction was then performed in the 1:3 molar ratio (run 3) and the reaction after usual workup afforded a 54:46 mixture of 1 and 2. As is evident from the above discussion, the reaction of complex 3 with bromine is a two-step process: the first step is the conversion of 3 to 1 and requires 2 equiv of bromine; the second step, which also requires 2 equiv of bromine, is the transformation of 1 to 2. It appears from these results that the first step is more preferred and the tetrabromide 2 is formed only when the amount of bromine used is more than 2 equiv. To check whether the transformation of 1 to 2 is a simple 1,4-addition of bromine to butadiene 1 or it is a palladium(II) bromide mediated reaction, we studied the reaction of complex 3 with iodine monobromide in different molar ratios (Table I). The results obtained were almost identical with those of bromine, thus eliminating the possibility of a 1,4-addition of bromine as no iodine monobromide addition product was obtained.

Besides the synthetic importance of the reaction, the selective transformation of complex 3 to 1 with 2 equiuv of bromine/iodine monobromide and to 2 with 4 equiv of bromine/iodine monobromide is quite significant from the mechanistic standpoint. A plausible mechanism for the transformations 3 → 2 → 1 is outlined in Scheme I. Nucleophilic substitution and addition reactions of the (π-allyl)palladium complex in the presence of stabilized

Scheme I



nucleophiles are well studied[14] and are believed to proceed through the coordination of ligand to the palladium in which the oxidation state of the palladium remains unchanged. We are engaged in the detailed mechanistic studies of these reactions which will be described at a later stage. On the basis of some of the observation, we propose a mechanism in which the initial step is the oxidation of 3 to (π-allyl)palladium(IV) complex (4) which readily decomposes to give 1 and $PdBr_2$. In the presence of excess of bromine/iodine monobromide, 1 is converted to 2. Although the possibility of a 1,4-addition cannot be ruled out completely, we believe that the second step is also mediated by the palladium halide liberated in the first step.

In conclusion, this note describes a simple, efficient, and high yield synthesis of two important synthetic intermediates from allene. Moreover, the reaction is significant from the industrial point of view as the recovery of $PdBr_2$ is almost quantitative. The possible intermediacy of the Pd(IV) species opens new facets to synthetic organic chemists, although many questions regarding the exact nature of this species remain to be answered.

Experimental Section

Melting points were determined on a Yamato capillary melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Varian VXR 200 high resolution spectrometer. Mass spectra were obtained on a Hewlett-Packard 5592B gas chromatograph–mass spectrometer. (π-Allyl)palladium complex (3) was prepared according to the Lupin et al. procedure.[12]

General Procedure for the Reaction of Complex 3 with Bromine/Iodine Monobromide. To a solution of complex 3 in a minimum quantity of chloroform was added appropriate amount of bromine/iodine monobromide under an argon atmosphere at room temperature. A solid soon started precipitating. The reaction mixture was stirred. The solid was filtered out, and the filtrate was washed with aqueous sodium carbonate, brine, and water, successively. The chloroform-soluble portion was dried over $MgSO_4$ and solvent evaporated to give crude product which was crystallized from hexane–ethyl acetate mixture. 1: mp 56–57 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 4.136 (s, 2 H), 4.162 (s, 2 H), 5.500 (s, 2 H), 5.532 (s, 2 H); MS (rel intensity), m/z 241.75 (4.4), 239.80 (8.7), 237.80 (4.6), 160.80 (100.0), 158.80 (96.9), 79.90 (16.1), 78.90 (62.7), 76.90 (47.7), 52.85 (12.1), 51.95 (10.8), 50.95 (14.0). 2: mp 158–159 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 4.134 (s); MS (rel intensity), m/z 401.70 (1.4), 399.70 (2.8), 397.70 (1.4), 322.80 (8.6), 320.80 (25.5), 318.80 (25.9), 316.85 (9.3), 240.80 (21.4) 238.85 (39.3), 236.85 (20.3), 160.85 (95.9), 158.85 (100.0), 79.95 (23.4), 78.95 (99.3), 78.00 (35.9), 77.00 (77.2), 52.95 (25.5), 51.95 (24.8), 50.95 (30.7), 49.95 (16.9).

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