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Abstract: High-yield reductive homocoupling of benzotrichloride and benzal chloride followed by consecutive reductive dechlorination to 1,2-dichlorostilbene and stilbene is effected in the presence of sodium formate as the reducing agent and Pd/C catalysts.

Keywords: Base, benzylic halides, homocoupling, Pd/C, reducing salts

INTRODUCTION

C-C bond formation via homo- or heterocoupling of alkyl and aryl halides is of considerable interest in modern organic synthesis.^[1] Stilbene and bibenzyl, which are used as intermediate compounds in the production of dyes, paints, and resins, are generally synthesized by homocoupling of benzyl halides in the presence of a stoichiometric excess of a metallic reducing

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agents. Commonly used agents include Ni,^[2] Mg,^[3] In,^[4] Fe,^[5] Mn coupled with CuCl₂,^[6] and Zn coupled with Cu^[7]; salts and carbonyl complexes^[8] of Ni, Co, V, Mo, and Fe have also been used. In a different approach, benzal chloride and benzotrichloride have been coupled and reduced to benzo-thiophenes when heated with sulfur^[9] at high temperature. With the exception of a recent report, which describes a catalytic electrochemical process,^[10] the various techniques disclosed hitherto for the coupling of benzylic halides all require the utilization of a stoichiometric amount of a reducing metal. However, having considered the environmental impact of the use and disposal of these toxic reducing reagents, there is incentive to find a cleaner catalytic alternative for these reactions.

We have previously demonstrated the unique activity of the Pd/C catalyst in the reductive homocoupling of aryl halides to biaryls in the presence of formate salts using water as the solvent.^[11] In this article, we describe the application of this scheme to the reductive coupling of benzyl chlorides to bibenzyl derivatives. The reaction is particularly effective for the coupling of benzal chloride and benzotrichloride to yield stilbenes.

RESULTS AND DISCUSSION

In a typical reaction, a mixture of 1.6 mmol of benzotrichloride (313 mg), 4 ml of dimethoxyethane (DME, solvent), 1.9 mmol of sodium formate (129 mg), 2.5 mmol of sodium carbonate (265 mg), 23.5 μ mol of 5% Pd/C catalyst (50 mg), and biphenyl (50 mg as an

$$2 \underbrace{\bigcirc}^{\text{CCI}_3}_{\text{Pd/C}, \text{DME}} + 2\text{HCO}_2\text{Na} + \text{Na}_2\text{CO}_3 \xrightarrow{120\ ^0\text{C}, 3\text{h}, 100\%}_{\text{Pd/C}, \text{DME}} \underbrace{\bigcirc}^{\text{(CI)C=C(CI)}}_{\text{I}, 87\%, \text{E/Z}-7/3} + 4\text{NaCI} + \text{H}_2\text{O}_2 \xrightarrow{(1)}_{\text{I}, 87\%, \text{E/Z}-7/3} + 3\text{CO}_2 \xrightarrow{(1)}_{$$

internal standard) was stirred at 120° C in a sealed pressure glass tube for 3 h. GC analysis of the reaction showed 100% conversion. 1,2-Dichloro-1,2-diphenylethylene (1, 87% GC yield, 7:3 E:Z ratio) with inorganic products, namely, sodium chloride, carbon dioxide, and water, were obtained (Eq. 1). Some toluene is formed as a result of competitive hydro-dehalogenation of the substrate.^[12]

The results are reproducible (Eq. 1) within 1.5% error margin and replicated exactly with almost the same results when scaled up to 10 times the original batch. The GC yield of **1** was around 85-86% at 100% conversion level. Similar results were obtained when 4-chlorobenzotrichloride was used as the substrate. Neither aryl-aryl bond formation nor aryl-alkyl bond formation were observed, suggesting that the benzyl C-Cl bonds are far more labile to the coupling process than the aromatic chlorides under these reaction conditions.

Benzylic Halides

The progress of reaction in Eq. (1), as monitored by GCMS, indicates that the formation of **1** is taking place in two consecutive steps: direct reductive coupling via activation of the benzylic C-Cl bond followed by reductive dehalogenation of the intermediate to yield **1**. The first step of the sequence was isolated from the rest by eliminating carbonate base from the reaction blend; the observed conversion rate was significantly slower and after 8 h of reaction time, an 85% yield of 1,1,2,2-tetrachloro-1,2-diphenylethane (**2**) along with 8% of **1** and 6% toluene were obtained. The process can be written as follows (Eq. 2):

The slow reaction rate in reaction 2 was attributed to the formation of hydrogen chloride, which affected the performance of the catalyst by reacting selectively with the active Pd(0) clusters.

The coupling product **2** was readily converted to **1** via reductive dehalogenation. Thus, heating **2** at 120° C for 3 h in the presence of formate and carbonate salts, DME, and Pd/C resulted quantitative yield of **1** (Eq. 3).

$$2 + HCO_2Na + 0.5Na_2CO_3 + \frac{120 \, {}^{0}C, 3h, 100\%}{Pd/C, DME} + (CI)C=C(CI)$$
2 - (CI)C=C(CI)
- 2NaCI
- 2NaCI
- 0.5II_2O
- 1.5CO_2 (3)

Comparable results were obtained when benzal chloride was treated under these conditions. Thus, when benzal chloride was exposed to the conditions of reaction 1 for 7.5 h, 61% stilbene (3) was obtained along with hydrolysis (benzaldehyde) and hydrogenolysis (toluene) products (Eq. 4) at 100% conversion level.

$$2 \underbrace{\bigcirc}^{\text{CHCl}_2} + 2\text{HCO}_2\text{Na} + \text{Na}_2\text{CO}_3 \xrightarrow{120\ ^{0}\text{C}, \ 7.5\text{h}, \ 100\%}_{\text{Pd/C}, \ \text{DME}} \bigotimes \xrightarrow{\text{CH=CH-}}^{\text{CH=CH-}} - 4\text{NaCl} + \text{H}_2\text{O} + 3\text{CO}_2$$
(4)

Analysis of the reaction mixture in the early stages of the reaction revealed that the expected intermediate, 1,2-dichloro-1,2-diphenylethane (4, Eq. 5) (1:1 dl/meso ratio), appeared momentarily (reaching a maximum of 42% after 3 h) and eventually converted to **3**.

$$2 \bigoplus^{\text{CHCl}_2} + \text{HCO}_2\text{Na} + 0.5 \text{ Na}_2\text{CO}_3 \xrightarrow{120^{\circ}\text{C}, 3\text{h}}{\text{Pd/C}, \text{DME}} \longrightarrow \bigoplus^{\text{C}(\text{CI})\text{H-C}(\text{CI})\text{H}}_{4, 42\%, \text{dl/meso}=1/1} \xrightarrow{+ 2\text{NaCI} + 0.5\text{H}_2\text{O} + 1.5\text{CO}_2} (5)$$

Benzyl chloride reacted in a similar way; however, it was found to be far more susceptible to the competing hydrogenolysis reaction, yielding toluene as the major product. As a result only 18% yield of bibenzyl (5) was obtained at complete benzyl chloride consumption level (Eq. 6).

$$2 \xrightarrow{\text{CH}_2\text{CI}} + \text{HCO}_2\text{Na} + 0.5\text{Na}_2\text{CO}_3 \xrightarrow{120\ ^0\text{C}, 7.5\text{h}, 100\%} + \text{CH}_2\text{-CH}_2\text{-CH}_2 \xrightarrow{\text{CH}_2\text{-CH}_2} \xrightarrow{\text{CH}_2\text{-CH}_2 - \text{CH}_2} \xrightarrow{\text{CH}_2\text{-CH}_2 - \text{CH}_2 - \text{CH}_$$

Even though a carbene mechanism was proposed previously for the metal-promoted coupling of benzotrichloride,^[3] we were unable to trap any of these intermediates using a cyclohexene scavenger. Evidently, addition of a radical scavenger such as hydroquinone significantly inhibited the progress of reactions 1, 2, 4, and 5; therefore, we propose that these reactions proceed via a single-electron transfer process resembling the mechanism we have put forward for the Pd/C-catalyzed reductive coupling of aryl halides in presence of formate salts.^[13] According to the latter, two neighboring palladium sites are oxidized through a one-electron transfer to the substrate, resulting in a chloride anion and an adsorbed α , α -dichlorobenzyl radical (Eq. 7):

$$2PhCCl_3 + Pd(0) \longrightarrow 2PhCCl_2 + Pd^{II}Cl_2$$
(7)

The radical species then dimerize to yield dibenzyl derivatives (Eq. 8):

$$\begin{array}{c} 2\text{Ph}\dot{C}\text{Cl}_2 \longrightarrow \text{Ph}(\text{Cl}_2)\text{C-C}(\text{Cl}_2)\text{-Ph} \\ 2 \end{array} \tag{8}$$

Finally, the Pd^{II} species is reduced by the formate salt to Pd^{0} , which initiates a new catalytic cycle: (Eq. 9):

$$Pd^{II}Cl_{2} + HCO_{2}Na + H_{2}O \longrightarrow Pd^{0} + 2HCl + NaHCO_{3}$$
(9)

The reduction with formate salts requires stoichiometric amount of water^[14] and no reaction (1-6) progress was asserted by GC unless a small amount of water was present in the system. However, once the reaction starts, water is generated in situ via neutralization of HCl with added carbonate base.

Interestingly, the reducing power of formate salt was further utilized in reaction 1 (Eq. 1) when four equivalents of it was added to the system and the mixture was maintained at 120°C for 20 h. The major product was identified as bibenzyl. We propose that a four-stage catalytic reductive cascade reaction is taking place in the following sequence (Eq. 10):

$$2PhCCI_{3} \xrightarrow{2e} Ph(CI_{2})C-C(CI_{2})Ph \xrightarrow{2e} Ph(CI)C=C(CI)Ph \xrightarrow{2H_{2}} PhCH-CHPh$$

$$3 \xrightarrow{1I_{2}} PhCH_{2}CII_{2}Ph$$

$$3 \xrightarrow{1I_{2}} PhCH_{2}CII_{2}Ph$$

$$-2HCI \qquad 5 \qquad (10)$$

Benzylic Halides

Reductive coupling in the first step is followed by reductive dehalogenation, which involves electron transfer from the metal to the substrates. Subsequently, the resulted dichlorostilbene undergoes hydrogenolysis in the third step followed by its hydrogenation to bibenzyl in the final step. The last two steps require hydrogen atoms; formate salt acts as the hydrogen donor.

EXPERIMENTAL

Melting points were measured in glass capillaries using an Electro thermal 9100 instrument. ¹H NMR spectra were measured on a Bruker AMX 300 instrument at 300.13 MHz. GC and GCMS analyses were performed using a HP-5890 gas chromatograph with a 50% diphenyl-50% dimethylpolysiloxane packed column ($25 \text{ m} \times 0.53 \text{ mm}$). Unless stated otherwise, chemicals were purchased from commercial vendors (>98% pure) and used as such without further purification. Products were either isolated and identified by comparison of their ¹H NMR spectra with standard samples, or identified by MS data and comparison of their GC retention times with standard samples.

1,2-Dichloro-1,2-diphenylethylene (1) was prepared by reducing 1,1,2,2-tetrachloro-1,2-diphenylethane (2). One mmol of 1,1,2,2-tetrachloro-1,2-diphenylethane (320 mg), 10 ml of THF, 2 mmol of sodium formate (136 mg), 2.5 mmol of sodium carbonate (265 mg), 3 mmol of water (54 mg), and 23.5 µmol of 5% Pd/C catalyst (50 mg) were mixed in a glass reactor and stirred under vigorous agitation at 120°C for several hours. After a stipulated period of time, the mixture was cooled and the solids were separated by filtration (the catalyst was washed several times with hot methanol and reused). The filtrate was distilled under reduced pressure to isolate the solvent from products. Crude 1,2-dichloro-1,2-diphenylethylene (1) (230 mg, 90% GC yields) was obtained, which, on recrystallization from methanol, gave 212 mg (85% isolated yield) of pure material. The isomers were separated by preparative chromatography. *cis*-Isomer Mp = $64-66^{\circ}$ C (pentane); NMR (CDCl₃) g 7.18 (s, Ar, 10 H). Anal. calcd. for C₁₄H₁₀Cl₂ (248.02): C, 67.49; H, 4.05; Cl, 28.46. Found: C, 67.45; H, 4.05; Cl, 28.50. *trans*-Isomer: Mp = $141-142^{\circ}$ C (ethanol); NMR (CDCl₃) g 7.30-7.75 (s, Ar, 10 H). Mass (m/z) 248, 233, 213, 195, 178, 152, 89. Anal. calcd. for C₁₄H₁₀Cl₂ (248.02): C, 67.49; H, 4.05; Cl, 28.46. Found: C, 67.45; H, 4.05; Cl, 28.50.

1,1,2,2-Tetrachloro-1,2-diphenylethane (2) was prepared by reacting 1.6 mmol of benzotrichloride (313 mg) in 4 ml of dimethoxyethane (DME, solvent) with 1.9 mmol of sodium formate (129 mg) in the presence of 23.5 μ mol of 5% Pd/C catalyst. The reaction mixture was stirred at 80°C for 8 h. An 85% yield of 1,1,2,2-tetrachloro-1,2-diphenylethane (2) along with 8% of 1 and 6% toluene was obtained by GC analysis. The reaction mixture was then cooled and filtered, and solvent evaporated under reduced

pressure to obtain 0.203 g (80% isolated yield) of crude 1,1,2,2-tetrachloro-1,2-diphenylethane, which upon recrystallization from acetic acid gave almost 180 mg of pure, white, crystal material, Mp 160–162°C; mass (m/z): 283, 247, 212, 195, 178, 159, 89. Anal. calcd. for $C_{14}H_{10}Cl_4$ (317.95): C, 52.49; H, 3.12; Cl, 44.32. Found: C, 52.48; H, 3.25; Cl, 44.00. NMR (CDCl₃) g 6.90–7.67 (m, Ar, 10 H).

trans-Stilbene (3) was synthesized from benzal chloride by refluxing a mixture of 1.9 mmol of benzal chloride (305 mg) in dimethylacetamide (DMA) solvent at 120°C oil-bath temperature in the presence of 1.9 mmol of sodium formate (129 mg), 2.5 mmol of sodium carbonate (265 mg), and 23.5 μ mol of 5% Pd/C catalyst. After 7.5 h, a 61% yield to *trans*-stilbene was obtained after workup and crystallization as stated previously. Mp 122–123°C; mass (m/z) 180, 165, 152, 115, 102, 89, 76, 63, 51. Anal. calcd. for C₁₄H₁₂ (180.09): C, 93.29; H, 6.71. Found: C, 93.25; H, 6.75.

1,2-Dichloro-1,2-diphenylethane (4) was prepared from benzal chloride by heating a mixture of 1.9 mmol of benzal chloride (305 mg), 1.9 mmol of sodium formate (129 mg), 2.5 mmol of sodium carbonate (265 mg), 23.5 μ mol of 5% Pd/C, and dimethylacetamide (DMA) for 3 h at 80°C. After workup, a 42% yield to product was realized. Mp 191–193°C; mass (m/z) 250, 215, 195, 178, 165, 152, 125, 115, 99, 89, 76, 63, 51. Anal. calcd. for C₁₄H₁₀Cl₂ (250.03): C, 66.95; H, 4.82; Cl, 28.23. Found: C, 67.45; H, 4.05; Cl, 28.50.

1,2-Diphenylethane (5) was synthesized from benzyl chloride by refluxing a mixture of dimethylacetamide (DMA), 1.9 mmol of benzyl chlorides (240 mg), 1.9 mmol of sodium formate (129 mg), 2.5 mmol of sodium carbonate (265 mg), and 23.5 μ mol of 5% Pd/C catalyst in a hot oil bath at 120°C. After 7.5 h, a 18% yield to product was obtained. Mp 51–52°C; mass (m/z) 182, 165, 152, 115, 104, 91, 77, 65, 51. Anal. calcd. for C₁₄H₁₄ (182.11): C, 92.26; H, 7.74. Found: C, 92.20; H, 7.77.

CONCLUSION

We have successfully demonstrated a simple, high-yield catalytic process for the coupling of α -halogenated toluenes to bibenzyls and stilbenes. The transformation of benzotrichloride to 1,2-diphenylethane is studied in detail and it is realized that the reaction proceeds in four distinct steps, starting with reductive coupling at the first step followed by reductive dehalogenation at the second, which involves electron transfer from the metals to the substrates. Subsequently, in the third step, the resulted dichlorostilbene undergoes hydrogenolysis followed by hydrogenation to bibenzyl in the final step, which can only occur in the presence of a hydrogen source such as formate salt. The reaction is selective and catalytic in Pd catalyst. Therefore, this work will certainly encourage chemists to eliminate toxic waste of excess metallic reducing agents previously used for this type of reaction.

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REFERENCES

- (a) Amatore, C.; Jutand, A. Anionic Pd (0) and Pd (II) intermediates in palladiumcatalyzed Heck and cross-coupling reactions. *Acc. Chem. Res.* 2000, *33* (5), 314–321; (b) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. Aryl-aryl bond formation one century after the discovery of the Ullmann reaction. *Chem. Rev.* 2002, *102* (5), 1359–1469; (c) Littke, A. F.; Fu, G. C. Palladium-catalyzed coupling reactions of aryl chlorides. *Angew. Chem., Int. Ed. Engl.* 2002, *41* (22), 4176–4211.
- Inaba, S.; Matsumoto, H.; Rieke, R. D. Highly reactive metallic nickel—reductive homocoupling reagent for benzylic monohalides and polyhalides. *J. Org. Chem.* 1984, 49 (12), 2093–2098.
- Ashby, E. C.; Alfekri, D. M. The reaction of benzotrihalides and benzal halides with magnesium—synthetic and mechanistic studies. *J. Organometal. Chem.* 1990, 390 (3), 275–292.
- Ranu, B. C.; Dutta, P.; Sarkar, A. Indium-promoted reductive homocoupling of alkyl and aryl halides. *Tetrahedron Lett.* 1998, 39 (51), 9557–9558.
- Ogata, Y.; Nakamura, H. A note on the dechlorination condensation of benzal chloride and benzotrichloride by iron and water. J. Org. Chem. 1956, 21 (10), 1170–1171.
- Ma, J.; Chan, T.-H. Organometallic-type reactions in aqueous media. Wurtzcoupling of alkyl halides with manganese/cupric chloride. *Tetrahedron Lett.* 1998, 39 (17), 2499–2502.
- de Sa, A. C. P. F.; Pontes, G. M. A.; dos Anjos, J. A. L.; Santana, S. R.; Bieber, L. W.; Malvestiti, I. Reductive coupling reaction of benzyl, allyl and alkyl halides in aqueous medium promoted by zinc. *J. Braz. Chem. Soc.* 2003, *14* (3), 429–434.
- (a) Hashimoto, I.; Tsuruta, N.; Ryang, M.; Tsutsumi, S. The reaction of potassium hexacyanodinickelate(1) with organic halides. J. Org. Chem. 1970, 35 (11), 3748–3752; (b) Yamada, Y.; Momose, D. Reductive coupling of benzylic halides by chlorotris(triphenylphosphine)cobalt(I). Chem. Lett. 1981 (9), 1277–1278; (c) Cooper, T. A. Reductive coupling of aralkyl halides by vanadium(II). J. Am. Chem. Soc. 1973, 95 (13), 4158–4162; (d) Yoshisato, E.; Tsutsumi, S. Reactions of benzyl halides with nickel carbonyl in various media. J. Org. Chem. 1968, 33 (2), 869–871; (e) Seyferth, D.; Millar, M. D. Reactions of dicobalt octacarbonyl and related compounds with gem-dihalides. J. Organomet. Chem. 1972, 38 (2), 373–383; (f) Coffey, C. E. Reaction of iron pentacarbonyl with gem-dihalides. J. Am. Chem. Soc. 1961, 83 (7), 1623–1626; (g) Alper, H.; Des Roches, D. Dehalogenation and condensation reactions of molybdenum carbonyls with activated halides. J. Org. Chem. 1976, 41 (5),

806–808; (h) Pinault, F. S.; Crumbliss, A. L. Cobaloxime(II)-initiated coupling of alpha, alpha, alpha-trihalomethylbenzenes. *J. Organomet. Chem.* **1981**, *215* (2), 229–239.

- 9. Geering, E. J. Benzothiophenes. US patent 3,278,552, Oct. 11, 1966.
- (a) Kaufman, S. A.; Phanijphand, T.; Fry, A. J. Cobalt (salen)-electrocatalyzed conversion of benzotrichloride into tolane. A triply catalytic and overall quintuple electrochemical transformation. *Tetrahedron Lett.* **1996**, *37* (45), 8105–8108; (b) Fry, A. J.; Singh, A. H. Cobalt (salen)-electrocatalyzed reduction of benzal chloride—dependence of products upon electrolysis potential. J. Org. Chem. **1994**, *59* (26), 8172–8177; (c) Nedelec, J. Y.; Perichon, J.; Troupel, M. Organic electroreductive coupling reactions using transition metal complexes as catalysts. *Top. Curr. Chem.* **1997**, *185*, 141–173 and reference cited therein.
- 11. (a) Mukhopadhyay, S.; Rothenberg, G.; Gitis, D.; Sasson, Y. Tandem one-pot palladium-catalyzed reductive and oxidative coupling of benzene and chlorobenzene. J. Org. Chem. 2000, 65 (10), 3107-3110; (b) Mukhopadhyay, S.; Rothenberg, G.; Wiener, H.; Sasson, Y. Palladium-catalyzed aryl-aryl coupling in water using molecular hydrogen: Kinetics and process optimization of a solid-liquid-gas system. Tetrahedron 1999, 55 (51), 14763-14768; (c) Mukhopadhyay, S.; Rothenberg, G.; Gitis, D.; Sasson, Y. On the mechanism of palladium-catalyzed coupling of haloaryls to biaryls in water with zinc. Org. Lett. 2000, 2 (2), 211-214; (d) Mukhopadhyay, S.; Rothenberg, G.; Joshi, A.; Baidossi, M.; Sasson, Y. Heterogeneous palladium-catalysed heck reaction of aryl chlorides and styrene in water under mild conditions. Adv. Synth. Catal. 2002, 344 (3-4), 348-354.
- Wiener, H.; Blum, J.; Sasson, Y. Studies on the mechanism of transfer hydrogenation of nitroarenes by formate salts catalyzed by Pd/C. J. Org. Chem. 1991, 56 (14), 4481–4486.
- Mukhopadhyay, S.; Rothenberg, G.; Gitis, D.; Wiener, H.; Sasson, Y. Kinetics and mechanism of heterogeneous palladium-catalyzed coupling reactions of chloroaryls in water. J. Chem. Soc., Perkin Trans. 2 1999, 2 (9), 2481–2484.
- 14. Wiener, H.; Sasson, Y.; Blum, J. Palladium-catalyzed decomposition of aqueous alkali-metal formate solutions. *J. Mol. Catal.* **1986**, *35* (3), 277–284.