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Facile reductive coupling of benzylic halides with ferrous oxalate dihydrate

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Facile reductive coupling of benzylic halides is reported with ferrous oxalate dihydrate in DMF or HMPA under nitrogen atmosphere at 155–160 °C. The coupling is proposed to proceed by two successive oxidative additions of benzylic halides to ferrous oxalate to give an intermediate organoiron complex which undergoes concerted dimerization to give the corresponding reductively coupled dimers in high yields.

Introduction

Reductive coupling of organic halides by metals, metal ions and metal complexes is of fundamental importance for the formation of carbon–carbon single bonds in organic synthesis. There are reports on reductive dimerization of benzylic halides with different metals and metal salts or complexes.[1] The reduction and/or coupling of halides by metals and metal ions/complexes can take place by atom transfer, electron transfer or oxidative addition.[1] Little is known about the role of the organometallic intermediates that are formed by oxidative addition of benzylic/aralkyl halides to low-valent transition metal compounds. The yields of coupled products depend on the specific halide, metal, ligands and reaction conditions used. Some of the reagents for reductive coupling of halides include $NiBr_2(PPh_3)_2$–Zn,[2] Pb–n-$Bu_4N^+Br^-$–DMF and $PbBr_2$–Al–DMF,[3] metallic nickel,[4] $Cp_2TiCH_2{\cdot}ZnI_2$,[5] $Ni(CO)_4$,[6] $W(CO)_6$,[7] and $Co_2(CO)_8$[8] *etc.* Among the iron metal salts and complexes, $Fe_3(CO)_{12}$–Pyr-*N*-oxide[9] is reported for the coupling of *p*-substituted benzyl chlorides to give 1,2-diphenylethanes in ~ 50% yield. Iron–water,[10] lithium chloroferrate,[11] $Na[Fe(CO)_2(C_5H_5)]$[12] and $Fe_3(CO)_{12}$[13] have also been found to be useful low valent coupling agents for benzylic halides.

While iron–water, $Fe_3(CO)_{12}$ and lithium chloroferrate could be used in different solvents such as water, acetonitrile, ethanol and tetrahydrofuran, the reactions were very slow and resulted in a mixture of oxygenated products besides the coupled product. Some of the reagents for reductive dimerization of benzylic halides (primary or secondary) are expensive, require hazardous conditions and give poor yields of the coupled products. Another major shortcoming of the methods discussed is insolubility of the reagent in the solvent. To overcome these disadvantages in the reactions of metal salts with organic halides, we decided to develop a simple and efficient method for reductive dimerization of benzylic halides using inexpensive ferrous oxalate dihydrate. One of its major advantages is its solubility in dimethylformamide (DMF) and hexamethylphosphoramide (HMPA) at elevated temperatures. This property of solubility of ferrous oxalate in DMF at elevated temperatures has already been utilized for reductive coupling of geminal dihalides to give olefins in high yields.[14]

Results and discussion

We report herein a novel method for the reductive coupling of benzylic halides with ferrous oxalate dihydrate in dry dimethylformamide (DMF) or hexamethylphosphoramide (HMPA) at 155–160 °C under nitrogen atmosphere to give the corresponding reductively coupled dimers in high yields. The reactions were complete in reasonable time (< 80 min) with both secondary and primary benzylic halides [eqn. (1)]. The

$$\underset{\mathbf{1a\text{-}p}}{\mathrm{ArRCHX}} \xrightarrow[\mathrm{N_2\ atm.,\ 155\text{-}160^{\circ}C}]{\mathrm{Iron(II)\ oxalate,\ HMPA/DMF}} \underset{\mathbf{2a\text{-}p}}{\mathrm{ArRCHCHRAr}} \qquad (1)$$

R = Aryl, H, Me and Et

coupled products were obtained in high yields using a 1 : 1 molar ratio of substrate to ferrous oxalate in the case of secondary benzylic halides. Primary benzylic halides required a 1 : 2 molar ratio of substrate to ferrous oxalate to give high yields of dimers. The reactions of primary benzylic halides were also complete using a 1 : 1 molar ratio of substrate to ferrous oxalate, but gave lower yields of the reductively coupled dimers as other undesired products were also obtained. Secondary benzylic bromides and chlorides were observed to react at nearly the same rate (runs 1 and 14, 6 and 10, 7 and 11), while the primary benzylic chlorides reacted more slowly than the corresponding bromides (runs 22 and 25, 23 and 26, 29 and 30). These results are summarized in Table 1.

9-Bromofluorene (**1a**) and chlorodiphenylmethane (**1c**) did not undergo any reaction with iron(II) oxalate in acetonitrile, THF or dioxane at reflux temperatures under nitrogen atmosphere. **1a** and **1c** underwent only methanolysis in methanol at reflux temperature and no coupled products were isolated. The reaction of **1a** and **1c** with iron(II) oxalate at 100 °C was sluggish and did not proceed to completion even after 3 h both in DMF and HMPA. Also, the starting halides were recovered unchanged quantitatively when stirred with iron(II) oxalate in DMF or HMPA at room temperature. The reactions of 9-bromofluorene (**1a**) with iron(II) chloride and iron(II) sulfate using a 1 : 0.5 molar ratio gave 32% and 51% of the dimer while reactions of chlorodiphenylmethane (**1c**) with iron(II) chloride and iron(II) sulfate under identical conditions yielded 20% and 57% of the coupled products only unlike reactions of **1a** and **1c** with iron(II) oxalate which gave nearly quantitative yields of dimers. This could be due to the insolubility of iron(II) chloride and iron(II) sulfate in DMF and HMPA even at elevated temperature.

The formation of dimers was also accompanied by the formation of alcohols and small amounts of carbonyl compounds in the case of primary benzylic halides and also with secondary benzylic halides when a lower molar ratio of substrate to Fe(II) was used. The formation of oxygenated products proceeds by competitive reactions of benzylic halides with DMF or HMPA, as confirmed by independent reactions of 9-bromofluorene (**1a**), bromodiphenylmethane (**1b**), chlorodiphenylmethane (**1c**), 1-bromomethylnaphthalene (**1k**) and 1-chloromethylnaphthalene (**1l**) with DMF or HMPA in the absence of ferrous oxalate which yielded corresponding alcohols and carbonyl compounds in varying ratios. 9-Bromofluorene (**1a**) showed the predominant formation of 9-(*N*,*N*-dimethylamino)fluorene

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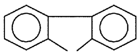
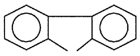
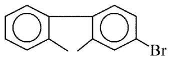
Table 1 Reactions of benzylic halides with iron(II) oxalate dihydrate in dry DMF or HMPA[a] at 155–160 °C under nitrogen atmosphere

Run no.	Substrate **1a–p**	Molar ratio **1a–p** : Fe(II)	Solvent	Time/min	Yield (%) Dimer	Yield (%) Alcohol	Mp/°C of dimer (**2**) Obs. (lit.)
1	**1a**	1 : 1	HMPA	10	87	—	246 (246–248[15])
2	**1a**	1 : 1	DMF	10	96	—	245 (246–248[15])
3	**1a**	1 : 0.5	HMPA	10	80	3[b,c]	246 (246–248[15])
4	**1a**	1 : 0.5	DMF	10	84	6[b,c]	246 (246–248[15])
5	**1a**	1 : 0.25	HMPA	10	57	7[b,c]	244 (246–248[15])
6	**1b**	1 : 1	HMPA	10	91	—	210 (210–212[16])
7	**1b**	1 : 1	DMF	10	95	—	210 (210–212[16])
8	**1b**	1 : 0.5	HMPA	10	89	—	210 (210–212[16])
9	**1b**	1 : 0.25	HMPA	10	50	42[c]	210 (210–212[16])
10	**1c**	1 : 1	HMPA	10	90	—	210 (210–212[16])
11	**1c**	1 : 1	DMF	10	92	—	210 (210–212[16])
12	**1c**	1 : 0.5	HMPA	10	93	—	210 (210–212[16])
13	**1c**	1 : 0.25	HMPA	10	58	26[c]	210 (210–212[16])
14	**1d**	1 : 1	HMPA	10	90	—	244 (246–248[15])
15	**1d**	1 : 0.5	HMPA	10	70	—[b,c]	245 (246–248[15])
16	**1e**	1 : 3	HMPA	10	70	—[c]	270 (272[17])
17	**1f**	1 : 1	HMPA	10	95	—	>325 (370[18])
18	**1g**	1 : 2	HMPA	30	54	10[c,d]	124 (126.7[19])[e]
19	**1h**	1 : 3	HMPA	30	43	23[c,d]	156–160 (160–161[20])[e]
20	**1i**	1 : 2	HMPA	30	37	26[c,d]	146 (147–148[21])[e]
21	**1j**	1 : 2	HMPA	30	42[d]	—	92 (92[22])[e]
22	**1k**	1 : 1	HMPA	20	42	48[c]	162–164 (162–163[23])
23	**1k**	1 : 1	DMF	60	31	52[c]	162–164 (162–163[23])
24	**1k**	1 : 2	HMPA	10	65	30[c]	160 (162–163[23])
25	**1l**	1 : 1	HMPA	60	70	15[c]	160 (162–163[23])
26	**1l**	1 : 1	DMF	120	42	41[c]	160 (162–163[23])
27	**1l**	1 : 2	HMPA	50	85	10[c]	160 (162–163[23])
28	**1m**	1 : 1	HMPA	40	39	46[c]	180 (183[23])
29	**1m**	1 : 2	HMPA	35	55	39[c]	181 (183[23])
30	**1n**	1 : 2	HMPA	80	66	19[c]	180 (183[23])
31	**1o**	1 : 2	HMPA	10	27	50[c]	175 (176–177[24])
32	**1o**	1 : 2	HMPA	10	37	46[c]	176 (176–177[24])
33	**1p**	1 : 2	HMPA	10	40	34[f]	112 (118[25])

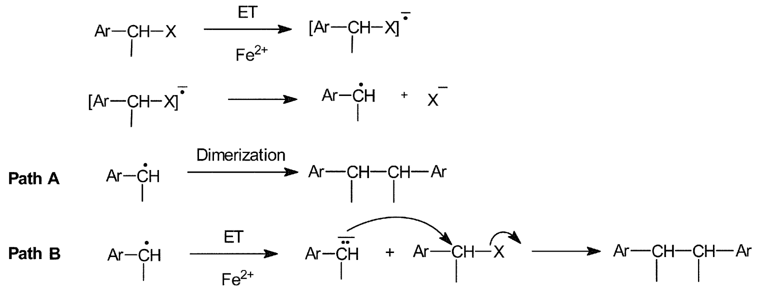
[a] ~ 50 mL of solvent/10 mmol of substrate. [b] 9,9′-Bifluorenylidene (10–13%) was also isolated. [c] Small amount of carbonyl compounds (2–8%) was also isolated. [d] Some other unidentified products were also obtained. [e] The products isolated were *meso* compounds. [f] 14% of corresponding carbonyl compound was also isolated.

Table 2

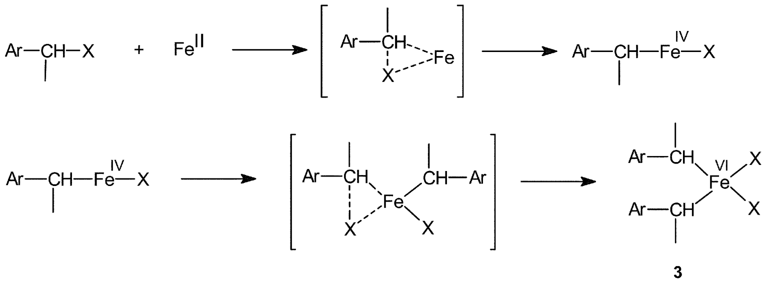
Substrate	Ar	R	X	Substrate	Ar	R	X
1a			Br	**1i**	4-ClC$_6$H$_4$	Me	Br
1b	Ph	Ph	Br	**1j**	Ph	Et	Br
1c	Ph	Ph	Cl	**1k**	1-naphthyl	H	Br
1d			Cl	**1l**	1-naphthyl	H	Cl
1e			Br	**1m**	2-naphthyl	H	Br
1f	4-ClC$_6$H$_4$	4-ClC$_6$H$_4$	Br	**1n**	2-naphthyl	H	Cl
1g	Ph	Me	Br	**1o**	2-Me-1-naphthyl	H	Br
1h	4-BrC$_6$H$_4$	Me	Br	**1p**	Mes	H	Br

besides 9-fluorenol and 9-fluorenone in blank reactions. The formation of oxygenated products and 9-(*N*,*N*-dimethylamino)-fluorene was greatly suppressed when reactions were carried out in the presence of ferrous oxalate. It is thus obvious that formation of alcohols and carbonyl compounds is due to competing reactions of the halides with DMF or HMPA even in the presence of ferrous oxalate. It is also inferred by a comparison of the results of blank reactions with reactions carried out in the presence of ferrous oxalate that formation of alcohols, carbonyl compounds and *N*,*N*-dimethylamino-substituted products is greatly suppressed or is completely eliminated when reactions are carried out with a higher molar ratio of ferrous oxalate. The primary benzylic halides invariably gave higher yields of oxygenated products. Among the primary benzylic halides, lower amounts of oxygenated products are obtained from chlorides compared to bromides due to slower nucleophilic substitution of chlorides by the oxygen end of DMF or HMPA. The amount of solvent also plays an important role since doubling the amount of solvent reduced the yield of coupled product and gave a higher yield of the oxygenated products.

The reaction of **1a** with sodium oxalate in HMPA at 155–160 °C did not show the formation of any dimeric product and only products corresponding to blank reactions were observed. Thence the formation of coupled products in the presence of iron(II) oxalate dihydrate must be due to the involvement of iron(II) rather than oxalate anion. The formation of the dimers can be conceived to proceed *via* radical coupling and/or nucleophilic attack of benzylic carbanion on halides (Scheme 1) which is initiated by electron transfer (ET) from iron(II). This possibility has, however, been eliminated, for the following



Scheme 1



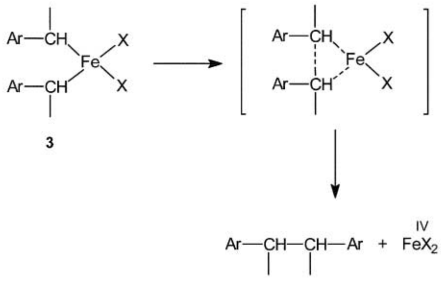
Scheme 2

reasons. (i) Firstly, if the above route was applicable to our reactions, a 1 : 1 molar ratio of the halide to iron(II) would be required for the completion of reactions. But we found that coupling was complete even in 1 : 0.5 molar ratio (runs 3, 4, 8, 12 and 15) of substrate to iron(II) oxalate and more than 50% of coupling has been observed with a 1 : 0.25 molar ratio (runs 5, 9 and 13). (ii) Secondly, the reaction of **1c** with iron(II) oxalate in the presence of 10 molar excess of cumene did not show the presence of any diphenylmethane. (iii) Thirdly, the radical cage, if formed at all, is not stable at such a high temperature and should escape to give reduced product (*e.g.* diphenylmethane). The absence of carbanions in our reactions was confirmed by the absence of diphenylmethane, when aliquots removed from the reaction mixture after 15, 30 and 45 min were quenched with acidified water.

All the reactions showed a distinctive change in the colour of the reaction mixture from yellow to greenish black or reddish orange within the first 5 min, which indicates formation of some sort of an organoiron complex. Since the reaction was complete even with half the molar equivalent of iron(II) and more than 50% of the reaction was complete with one-fourth molar equivalent of iron complex (runs 3, 4, 5, 8, 9, 12, 13 and 15), it suggests that the organoiron complex involves at least two halide molecules for each iron(II) species. The higher amounts of the coupled products obtained than expected from a 1 : 0.25 molar ratio could be due to various redox reactions which regenerate iron(II) for further coupling.

In view of the above arguments, it is likely that the proposed organoiron complex could arise by a non-radical oxidative addition by two successive three-centre, concerted, frontside nucleophilic displacements (Scheme 2).[1] It is noteworthy in this connection that in a recent study on the reductive coupling of benzylic chlorides in the presence of $Fe_3(CO)_{12}$ in benzene, a broad signal at δ 1.22 ppm assignable to the methylene group of the unstable system $PhCH_2Fe$ was recorded.[9]

The dimeric products could arise from the organoiron complex **3** by a homolytic process in the solvent cage but a cage reaction, if occurring, at the temperature of our reactions (*i.e.* 155–160 °C) would have allowed a part of the radicals to diffuse out of the cage and as a consequence some diphenylmethane would have been obtained. The absence of diphenylmethane and the absence of cross coupled product suggest that the homolytic cleavage of the organoiron complex **3** does not take place. In our opinion, the proposed organoiron complex **3** undergoes a facile, concerted process [eqn. (2)] to give the dimeric products as is known for two alkyl ligands attached to a single metal centre.[26]



(2)

The iron species in higher oxidation states could be converted to lower oxidation states by various permissible redox reactions. The distinct colour change, stoichiometry of the reaction, absence of radical-derived products and absence of carbanions in these reactions support the proposed pathway for reductive coupling of benzylic halides with ferrous oxalate in dry DMF or HMPA at 155–160 °C under nitrogen atmosphere. The formation of carbocations is inconceivable as this would have led to the formation of oxygenated products in high yields due to competitive coupling with solvent molecules. Also higher amounts of oxygenated products would have been obtained from secondary benzylic halides compared to primary benzylic halides which is contrary to our observations. We conclude that benzylic halides can be reductively coupled with inexpensive ferrous oxalate dihydrate in DMF or HMPA at 155–160 °C to give high yields of the dimers.

Experimental section

Melting points were recorded on a Tropical labequip apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR SPECTRUM-2000 instrument. NMR spectra were recorded on an FT-NMR model R-600 Hitachi (60 MHz) instrument with TMS as the internal standard. HMPA and DMF[27] were dried by allowing them to stand over calcium oxide for 24 h followed by filtration and distillation under vacuum. (**Caution:** DMF vapours are harmful, irritating to skin, eyes, and mucous membranes. DMF is suspected to be a carcinogen and must be used in a fume hood. HMPA is an industrial substance suspected of having carcinogenic potential for man. Adequate precautions must be taken to avoid all forms of exposure to HMPA). The solvents were deaerated by bubbling nitrogen into the solvent. Ferrous oxalate dihydrate was used as such. 9-Bromofluorene,[28] bromodiphenylmethane,[28] 2,9-dibromofluorene,[29] 1-bromomethylnaphthalene,[30] 2-bromomethylnaphthalene,[31] α-bromoethylbenzene, *p*,α-dibromoethylbenzene, *p*-chloro-α-bromoethylbenzene and α-bromopropylbenzene were prepared by allylic bromination with *N*-bromosuccinimide. Bis(*p*-chlorophenyl)bromomethane[32] was prepared by reaction of HBr with *p*,*p*′-dichlorobenzhydrol. 1-Bromomethyl-2-methylnaphthalene[33] and bromomethylmesitylene[34] were prepared by bromomethylation of 2-methylnaphthalene and mesitylene, respectively. 9-Chlorofluorene[35] was prepared by treatment of 9-fluorenol with HCl. 1-Chloromethylnaphthalene[36] was prepared by chloromethylation of naphthalene and 2-chloromethylnaphthalene[37] was prepared by refluxing 2-hydroxymethylnaphthalene with thionyl chloride in toluene.

General procedure

In a dried, N_2-filled three-necked round bottomed flask, mounted over a magnetic stirrer and fitted to a reflux condenser and mercury trap, was placed a mixture of halide (2.5 mmol), iron(II) oxalate dihydrate (according to Table 1) and dry deaerated DMF or HMPA (12.5 mL). The system was deaerated by flushing with N_2 for 10 min. The contents of the flask were heated in an oil-bath maintained at 155–160 °C. A distinct colour change to greenish black or orangish red was observed during the first 5 min. The progress of the reaction was monitored by TLC (eluent: petroleum ether (60–80 °C)–ethyl acetate). After complete disappearance of starting material, the mixture was allowed to cool to room temperature and poured in 0.5 M H_2SO_4 (100 mL). A white or creamish white solid was obtained in runs 1, 2, 6, 7, 8, 10, 11, 12 and 14. The solid was filtered at the pump and dried under vacuum. The product was pure as checked by TLC and was identified by mp, mixed mp (wherever applicable), IR and NMR spectra.

The crude product mixtures in the rest of the reactions were extracted with diethyl ether (3 × 15 mL). The combined ethereal extract was washed with water (20 mL) and dried over anhyd. $MgSO_4$. The solvent was removed on a Buchi rotavapor and the residue was chromatographed on a silica gel column (100–200 mesh) using petroleum ether–ethyl acetate as the eluent. The isolated products were concentrated and dried under vacuum. The products were identified by mp, mixed mp (wherever applicable), IR and NMR spectra.

Reactions of benzylic halides with HMPA or DMF

The reactions of benzylic halides (2.5 mmol) with HMPA or DMF (12.5 mL) were carried out in the absence of ferrous oxalate at 155–160 °C under nitrogen atmosphere. The progress of the reactions was monitored by TLC. The reactions were worked up by cooling the flask to room temperature and pouring the mixture into ice cold water (50 mL). The crude product mixture was extracted with diethyl ether (2 × 25 mL), dried (anhyd. $MgSO_4$) and concentrated on a rotary evaporator. The concentrate was chromatographed on a silica gel column (100–200 mesh) using petroleum ether–ethyl acetate as eluent. The isolated products were characterized by mp, NMR and IR spectra.

Reaction of chlorodiphenylmethane (1c) with Fe(II) oxalate dihydrate in the presence of cumene

The reaction of chlorodiphenylmethane (2.5 mmol), ferrous oxalate (2.5 mmol) and cumene (25 mmol) in dry HMPA (12.5 mL) was carried out as above in an oil bath maintained at 155–160 °C under nitrogen atmosphere. The starting material disappeared completely after 10 min, as observed by TLC using petroleum ether–ethyl acetate (95 : 5, v/v) as eluent. The reaction mixture was quenched with 0.5 M H_2SO_4 (100 mL) after 60 min and work up as above. Close examination of the reaction mixture showed a complete absence of diphenylmethane. 1,1,2,2-Tetraphenylethane (91%) was isolated as confirmed by mp and mixed mp.

Acknowledgements

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