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Reductive Dimerization of Allyl and Benzyl Halides in Pb/n-Bu$_4$NBr–DMF and PbBr$_2$/Al–DMF Systems

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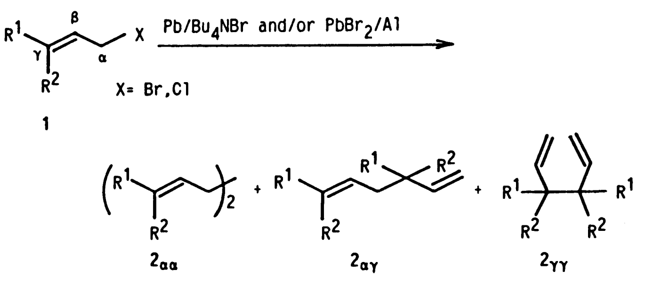
Synopsis. Reductive dimerization of allyl and benzyl halides has been performed by treatment with Pb/n-Bu$_4$NBr and catalytic PbBr$_2$/Al in *N,N*-dimethylformamide.

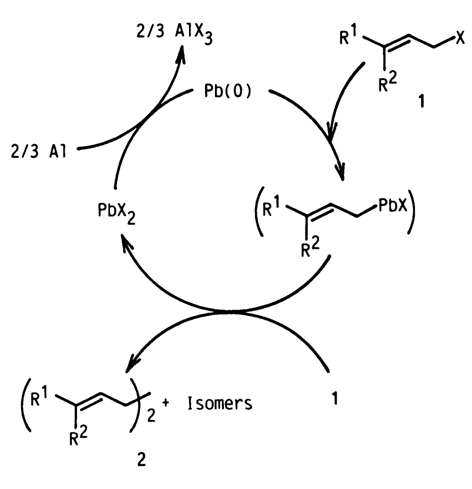
Reductive coupling of organic halides is of importance for making carbon–carbon linkage in organic synthesis. Various metals, e.g., Cu,[1] Te,[2] Mo,[3] Fe,[4,5] Zn,[6] V,[7] Sm,[8] Co,[9] and Ni,[10,11] have been utilized for the reductive dimerization of allyl and benzyl halides. The combination of metal halides, e.g., TiCl$_3$,[12] VCl$_3$,[13] CrCl$_3$,[14] and WCl$_6$,[15] with LiAlH$_4$ has also proved to be useful. However, many of these reagents require scrupulous attention and/or hazardous conditions to use. Meanwhile, lead is still untouched for this purpose, presumably due to the lack of suitable reaction media for the generation of organolead reagents.[16] Recently, we have reported an effective lead-promoted "Barbier-type" reaction, wherein the combination of lead with tetrabutylammonium bromide (n-Bu$_4$NBr) in *N,N*-dimethylformamide (DMF) is quite effective for the generation of the intermediary active lead species for the allylation of carbonyl compounds.[17] Furthermore, we have found a new lead(0)-recycling system for the allylation of carbonyl compounds, which has been successfully performed with a combination of catalytic PbBr$_2$ and Al.[18]

In the lead-promoted allylation of carbonyl compounds, especially less reactive carbonyl compounds, an excess amount of allyl bromide was required to complete the reaction.[17] Notably, when allyl bromide was treated with lead in DMF prior to treatment with carbonyl compounds, any appreciable amount of the allylation products was not obtained. These facts suggest that the reductive dimerization of allyl bromide takes place competitively and, in turn, enable us to investigate allyl–allyl coupling in the Pb/n-Bu$_4$NBr–DMF and PbBr$_2$/Al–DMF systems. Herewith, we describe that both the unique combinations of Pb/n-Bu$_4$NBr and PbBr$_2$/Al are effective for the reductive dimerization of a variety of allyl and benzyl halides at ambient temperature.



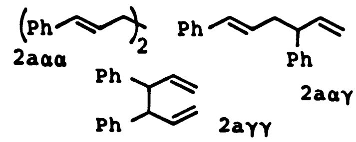
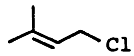
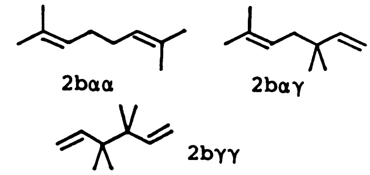
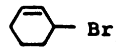
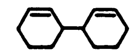
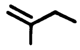
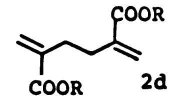
Scheme 1.

Reductive Dimerization in a Pb/n-Bu$_4$NBr System (Method A). The reductive dimerization of a variety of allyl and benzyl halides in a Pb/Bu$_4$NBr system took place to give the corresponding coupling products (Table 1). Thus, into a stirred mixture of cinnamyl bromide (**1a**, X=Br), n-Bu$_4$NBr, and trimethylsilyl chloride (Me$_3$SiCl) in DMF was immersed a Pb plate. The reaction was continued at ambient temperature until most of **1a** was consumed (Entry 1). After taking out the Pb plate (loosing ca. 0.5 equiv. Pb), usual workup of the mixture afforded the corresponding dimers **2a** (73%). The addition of Me$_3$SiCl was indispensable for initiation of the reaction. However, when the Pb plate was treated with aqueous 5% HCl and air-dried immediately before use, the reaction took place similarly without addition of Me$_3$SiCl (yield; 72%), suggesting that the addition of Me$_3$SiCl and/or HCl liberated in situ would effect the activation of Pb plate surface. The effect of n-Bu$_4$NBr was remarkable; in the absence of n-Bu$_4$NBr, the reductive dimerization of allyl halides scarcely occurred except for **1a** (X=Br) (Entries 1 and 4 in Table 1). When n-Bu$_4$NBr was replaced with other salts, the yield of coupling products of cinnamyl chloride (**1a**, X=Cl) decreased in the order: n-Bu$_4$NBr(63%)>NaBr(50%)>C$_6$H$_5$CH$_2$N(CH$_3$)$_3$Br(none). Although the role of n-Bu$_4$NBr in the reductive dimerization is still unclear, it is likely that n-Bu$_4$NBr effects the generation of an active organolead reagent, e.g., n-Bu$_4$NPb·[19] and (n-Bu$_4$N)(PbBr$_2$(CH$_2$CH=CH$_2$)).[20] The effect of solvent is also remarkable since the yield of coupling products of **1a** (X=Br) varies significantly



Scheme 2.

Table 1. Reductive Dimerization of Allyl and Benzyl Halides[a)]

Entry	Halide	Method[b)]	Time[c)] / h	Product	Yield[d)] / %
1	 1a (X= Br)	A	14	 2aαα 2aαγ 2aγγ	$73^{e)}$ (83)
2	1a (X= Br)	B_1	24	2a	$90^{e)}$
3	1a (X= Br)	B_2	14	2a	$85^{e)}$
4	1a (X= Cl)	A	14	2a	$63^{e)}$ (-)
5	1a (X= Cl)	B_1	$2^{f)}$	2a	$54^{e)}$
6	1a (X= Cl)	B_2	15	2a	$72^{e)}$
7	1a (X= Cl)	B_3	19	2a	$74^{e)}$
8	 1b	A	24	 2bαα 2bαγ 2bγγ	$60^{g)}$
9	 1c	A	3	 2c	$100^{h)}$
10	 1d COOR (R= Me)	A	4	 2d (R= Me)	60
11	1d (R= Me)	B_1	10	2d (R= Me)	62
12	1d (R= Et)	B_1	15	2d (R= Et)	71
13	$PhCH_2Br$ 3	A	$4^{f)}$	$PhCH_2CH_2Ph$ 4	50
14	3	B_1	24	4	37
15	Ph_2CHBr 5	B_1	30	$Ph_2CHCHPh_2$ 6	67

a) Carried out at ambient temperature. b) A: With Pb/*n*-Bu_4NBr/Me_3SiCl in DMF; B_1: With $PbBr_2/Al$ in DMF; B_2: with $PbBr_2/Al$ in THF; B_3: with $PbBr_2/Al$ in THF-H_2O (1:1). c) Unless otherwise noted, the reaction was continued until most of halides (1 mmol) were consumed. d) Isolated yields; numbers in parentheses showing the yields of coupling products obtained in the absence of *n*-Bu_4NBr. e) **2aαα/2aαγ/2aγγ** ratio of ca. 2:2:1 (^1H NMR and/or GLPC). f) Carried out at 60—65 °C. g) **2bαα/2bαγ/2bγγ** ratio of 77:20:3 (^1H NMR and/or GLPC). h) meso/dl ratio of 1:1 (GLPC).

depending on the choice of the solvent: DMF(73%)> MeCN(27%)>CH_2Cl_2(trace)>THF(none), MeOH(none).

The coupling products **2a** and **2b** were mixtures of three regio-isomers (**2aαα**/**2aαγ**/**2aγγ** ratio: ca. 2/2/1 (Entries 1—7); **2bαα**/**2bαγ**/**2bγγ** ratio: ca. 77/20/3 (Entry 8)).[21)] The product **2c** was a mixture of the corresponding meso and dl isomers in a ratio of 1:1 (Entry 9). The yield of the reductive dimerization of benzyl bromide (**3**) was not satisfactory (yield, 9%), but was improved to some extent (up to 50% yield) when the reaction was carried out at higher temperature (60—65 °C, Entry 13).

Reductive Dimerization in a $PbBr_2$/Al System (Method B). Furthermore, we found that the reductive dimerization of allyl and benzyl halides was successfully performed with the combination of $PbBr_2$ (7 mol%) and Al foils (1 equiv.) in DMF. The representative results are summarized in Table 1 (Method B_{1-3}). The reductive dimerization of **1a** (X=Br, Cl) in the $PbBr_2$/Al-DMF system took place smoothly (Entries 2 and 5). The satisfactory results were also obtained when the reaction was operated in THF (Entries 3 and 6) and THF-H_2O (1:1) (Entry 7). In a similar manner, the reaction of α-(bromomethyl)-acrylic esters **1d** (R=Me, Et), **3**, and bromodiphenylmethane (**5**) afforded the corresponding coupling products (Entries 11, 12, 14, and 15) respectively.

Although the details on the mechanism of the

$PbBr_2$/Al-promoted reductive dimerization have not been clarified yet, this system seems to involve the regeneration of Pb(0) by the reduction of $PbBr_2$ with Al (Scheme 2). The Pb(0) generated in this way would effect the reductive dimerization of the halides, since in the absence of $PbBr_2$ no appreciable coupling products were obtained. Further applications of the $PbBr_2$/Al system are in progress and will be reported in due course.

Experimental

IR spectra were taken on a JASCO IRA-1 grating spectrometer. ^1H NMR spectra were obtained on a Hitachi R-24 (60 MHz) and/or JEOL FX-100 (100 MHz), and ^{13}C NMR spectra on a JEOL FX-100 (25.05 MHz) spectrometer. Chemical shifts are expressed in parts per million downfield from Me_4Si used as internal standard. Analytical gas chromatography was carried out on a Yanaco GCG-550T using a column packed with Silicone SE-30 (10%) on Chamelite CK.

Materials. Cinnamyl halides (**1a**) (X=Br, Cl), 1-chloro-3-methyl-2-butene (**1b**), 3-bromocyclohexene (**1c**), benzyl bromide (**3**), and bromodiphenylmethane (**5**) were purchased from Tokyo Kasei Kogyo Co., LTD. and used as received. Methyl and ethyl α-(bromomethyl)acrylates (**1d**) (R=Me, Et) were prepared according to the method described in the literature.[22]

General Procedure of the Reductive Dimerization. A typical reaction procedure is as follows.

Method A: Into a stirred mixture of cinnamyl bromide (**1a**, X=Br) (1 mmol), n-Bu_4NBr (1 mmol), and Me_3SiCl (0.2 ml) in DMF (6 ml) was immersed a Pb plate (>99.9%; 1.5×2.0 cm^2, 0.5 mm thick) and the stirring was continued at ambient temperature until most of **1a** was consumed (14 h). After taking out the Pb plate (loosing ca. 0.5 mmol of Pb), the mixture was quenched with aqueous 5% HCl and extracted with AcOEt (6 ml×5). The extracts were washed with aqueous $NaHCO_3$ (6 ml) and brine (6 ml×4), dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, hexane-AcOEt (3:1)) to give a mixture of the corresponding dimers **2a** (73%), whose GLPC analysis showed the presence of three regio-isomers **2a**$\alpha\alpha$, **2a**$\alpha\gamma$, and **2a**$\gamma\gamma$ in a ratio of 39:43:18. Identification of the products was performed by comparison of its IR, ^1H NMR, and/or ^{13}C NMR spectra with reported ones.[2]

Method B: Into a mixture of $PbBr_2$ powders (0.07 mmol) and finely cut Al foils (1 mmol) in DMF (5 ml) was added cinnamyl bromide (**1a**, X=Br) (1 mmol) and the mixture was stirred at ambient temperature until most of **1a** was consumed (24 h). The unreacted Al foils were separated and the reaction mixture was worked up in a similar manner to that described above. The corresponding dimers **2a** were obtained in 90% yield. GLPC analysis of the products showed the presence of three regio-isomers **2a**$\alpha\alpha$, **2a**$\alpha\gamma$, and **2a**$\gamma\gamma$ in a ratio of 40:41:19 (Method B_1). In a similar manner, the reductive dimerization of cinnamyl chloride (**1a**, X=Cl) (1 mmol) with $PbBr_2$ (0.07 mmol)/Al (1 mmol) in THF (Method B_2) and THF-H_2O (1:1) (Method B_3) afforded the dimers **2a** in 72 and 74% yields, respectively. GLPC analysis of these products showed the presence of three regio-isomers (the ratio of 41:40:19 and 35:43:22).

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