Alkylpotassium-Catalyzed Benzylic C–H Alkylation of Alkylarenes with Alkenes

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Supporting Information

General

$^1$H and $^{13}$C NMR spectra were recorded on JEOL JNM-ECA500 and JNM-ECX600 spectrometers in CDCl$_3$ unless otherwise noted. Tetramethylsilane (TMS) served as internal standard (δ= 0) for $^1$H NMR, and CDCl$_3$ served as internal standard (δ= 77.0) for $^{13}$C NMR. Benzo trifluoride (BTF) served as internal standard (δ= –63.72) for $^{19}$F NMR. IR spectra were measured by JASCO FT/IR-4200 spectrometer. Preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F. Potassium tert-butoxide (KO$_{tBu}$) was purchased from Wako Pure Chemical Industries, Ltd. Lithium 2,2,6,6-tetramethylpiperidizide (LiTMP) was purchased from Aldrich Co., Ltd. (Trimethylsilyl)methyl potassium (KCH$_2$TMS) was prepared according to the literature.$^1$ N,N,N′,N′-Tetramethylethlenediamine (TMEDA) and N,N,N″,N″-pentamethyldiethylenetriamine (PMDTA) were purchased from Tokyo Chemical Industry Co., Ltd. Heptane was purchased from Tokyo Chemical Industry Co., Ltd., and distilled just before using in the presence of benzophenone and sodium. Alkylarenes were purchased from Tokyo Chemical Industry Co., Ltd., and distilled with CaH. 2’, 2a were purchased from Tokyo Chemical Industry Co., Ltd., and distilled with CaH. 2b, 2c, 2d, 2e, 2f, 2j, 2i, 2g, 2h were synthesized according to the literatures. 2h, 2g and 2h were synthesized by typical Wittig reaction between corresponding aldehydes and benzyltriphenylphosphonium bromide, and data are in accordance with the literatures.

Typical procedure for catalytic addition reaction of alkylarenes 1 with Alkene 2 (Condition A, The reaction in Scheme 2, entry 1 as a model)

KCH$_2$TMS (3.8 mg, 3.0 x 10$^{-2}$ mmol) and alkene 2a (540.4 mg, 3.0 mmol) were placed in a flame-
dried 20 mL flask inside a glove box fulfilled with argon, and alkylarene 1a (7.5 mL) and PMDTA (6.3 µL, 3.0 x 10^-2 mmol) was subsequently added at −78 °C via well-dried syringe, and the whole mixture was stirred for 24 h at 0 °C. The reaction was quenched by adding water (2.0 ml) and extracted with DCM (20 mL x 3). The combined organic layer was dried over anhydrous Na2SO4. After filtration and concentration under reduced pressure, the crude product obtained was purified by flash column chromatography on silica gel (Hexane/DCM = 20:1) to afford the desired product 3aa (710.1 mg, 2.61 mmol, 87% yield).

Typical procedure for catalytic addition reaction of alkylarenes 1 with alkene 2 (Condition B, The reaction in Scheme 2, entry 2 as a model)

KCH₂TMS (3.8 mg, 3.0 x 10⁻² mmol) and alkene 2a (271.0 mg, 1.5 mmol) were placed in a flame-dried 10 mL flask inside a glove box fulfilled with argon, and CPME (0.75 ml), alkylarene 1b (0.75 mL, 1.2 x 10 mmol, 4.0 eq.) and PMDTA (6.2 µL, 3.0 x 10⁻² mmol) was subsequently added at −78 °C via well-dried syringe, and the whole mixture was stirred for 18 h at 0 °C. The reaction was quenched by adding water (2.0 ml) and extracted with DCM (20 mL x 3). The combined organic layer was dried over anhydrous Na2SO4. After filtration and concentration under reduced pressure, the crude product obtained was purified by PTLC (Hexane/DCM = 8:1 x 3) to afford the desired product 3ba (351.6 mg, 1.16 mmol, 78% yield).

References

NMR Charts

Propane-1,2,3-triyltribenzene (3aa)
Propane-1,2,3-triyltribenzene (3aa)
(3-(2-Methoxyphenyl)propane-1,2-diyl)dibenzene (3ba)
(3-(2-Methoxyphenyl)propane-1,2-diyl)dibenzene (3ba)
(3-(3-Methoxyphenyl)propane-1,2-diyl)dibenzene (3ca)
(3-(3-Methoxyphenyl)propane-1,2-diyl)dibenzene (3ca)
(3-(3-Methoxy-5-methylphenyl)propane-1,2-diyl)dibenzene (3da)
(3-(3-Methoxy-5-methylphenyl)propane-1,2-diyl)dibenzene (3da)
3-(2-Fluorophenyl)propane-1,2-diyl) dibenzene (3ea)
3-(2-Fluorophenyl)propane-1,2-diyl)dibenzene (3ea)
3-(2-Fluorophenyl)propane-1,2-diyl)dibenzene (3ea)
(3-(3-Fluorophenyl)propane-1,2-diyldibenzene (3fa)
(3-(3-Fluorophenyl)propane-1,2-diyl)dibenzene (3fa)
(3-(3-Fluorophenyl)propane-1,2-diyl)dibenzene (3fa)
(3-<i>o</i>-Tolyl)propane-1,2-diyl)dibenzene (3ga)
(3-(o-Tolyl)propane-1,2-diyl)dibenzene (3ga)
(3-(m-Tolyl)propane-1,2-diyl)dibenzene (3ha)
(3-(m-Tolyl)propane-1,2-diyl)dibenzene (3ha)
(3-(p-Tolyl)propane-1,2-diyl)dibenzene (3ia)
(3-(p-Tolyl)propane-1,2-diyl)dibenzene (3ia)
(3-(4-Isopropylphenyl)propane-1,2-diyl)dibenzene (3ja)
(3-(4-Isopropylphenyl)propane-1,2-diyl)dibenzene (3ja)
(Butane-1,2,3-triyl)tribenzene (major diastereomer, 3ka-M)
(Butane-1,2,3-triyl)tribenzene (major diastereomer, 3ka-M)
(Butane-1,2,3-triyl)tribenzene (minor diastereomer, 3ka-m)
(Butane-1,2,3-triyl)tribenzene (minor diastereomer, 3ka-m)
4,4'-[(3-Phenylpropane-1,2-diyl)bis(tert-butylbenzene)] (3ab)
4,4'-((3-Phenylpropane-1,2-diyl)bis(tert-butylbenzene) (3ab)
3,3'-(3-Phenylpropane-1,2-diyl)bis(methoxybenzene) (3ac)
3,3'-(3-Phenylpropane-1,2-diyl)bis(methoxybenzene) (3ac)
4,4'-(3-Phenylpropane-1,2-diyl)bis(methoxybenzene) (3ad)
4,4'-(3-Phenylpropane-1,2-diyl)bis(methoxybenzene) (3ad)
$1,1'-(3$-Phenylpropane-1,2-diyl)dinaphthalene (3ae)$
1,1'-(3-Phenylpropane-1,2-diyl)dinaphthalene (3ae)
(2-(4-Methoxyphenyl)propane-1,3-diyl)dibenzene (3af)
(2-(4-Methoxyphenyl)propane-1,3-diyl)dibenzene (3af)
1-Methoxy-2-(2-(4-methoxyphenyl)-3-phenylpropyl)benzene (3bf)
1-Methoxy-2-(2-(4-methoxyphenyl)-3-phenylpropyl)benzene (3bf)
1-Methoxy-3-(2-(4-methoxyphenyl)-3-phenylpropyl)benzene (3cf)
1-Methoxy-3-(2-(4-methoxyphenyl)-3-phenylpropyl)benzene (3cf)
(2-(2-Methoxyphenyl)propane-1,3-diyl)dibenzene (3ag, mixture of regioisomers)
(2-(2-Methoxyphenyl)propane-1,3-diyl)dibenzene (3ag, mixture of regioisomers)
1-(2,3-Diphenylpropyl)naphthalene (3ah)
1-(2,3-Diphenylpropyl)naphthalene (3ah)
(2-Propylpropane-1,3-diyl)dibenzene (3ai)
(2-Propylpropane-1,3-diyl)dibenzene (3ai)
(2-Isopropylpropane-1,3-diyl)dibenzene (3aj)
(2-Isopropylpropane-1,3-diyl)dibenzene (3aj)
Triphenyl(3-phenylpropyl)silane (5aa)
Triphenyl(3-phenylpropyl)silane (5aa)
Dimethyl(phenyl)(3-phenylpropyl)silane (5ab)
Dimethyl(phenyl)(3-phenylpropyl)silane (5ab)
(3-(3-Methoxyphenyl)propyl)dimethyl(phenyl)silane (5cb)
(3-(3-Methoxyphenyl)propyl)dimethyl(phenyl)silane (5cb)