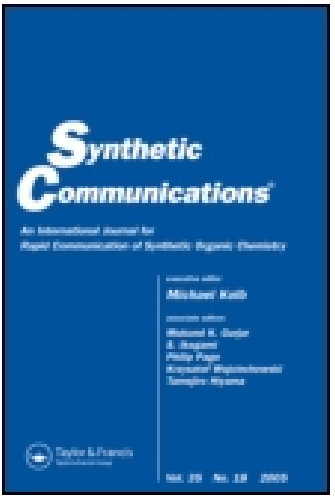

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Gallium Mediated Allylation and Propargylation of 1-(α-Aminoalkyl)benzotriazole: An Alternative Route to Homoallylic and Homopropargyl Amines

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GALLIUM MEDIATED ALLYLATION AND PROPARGYLATION OF 1-(α -AMINOALKYL)-BENZOTRIAZOLE: AN ALTERNATIVE ROUTE TO HOMOALLYLIC AND HOMOPROPARGYL AMINES

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Abstract: Mediated by gallium metal 1-(α -aminoalkyl)benzotriazole reacted with allylic and propargyl bromide to give homoallylic and homopropargyl amines in moderate to good yields.

Recently Barbier-type reaction has received considerable interest as an one-step alternative to the Grignard reaction, owing to the development of several modifications which expand its synthetic potential. The use of metals alternative to magnesium, such as lithium,[1] zinc,[2] bismuth,[3] indium,[4] lead,[5] has been investigated. Ultrasound irradiation has been found to improve yields. The reactions which have been promoted by above metals are comparatively extensive. Compared to other metals, gallium has not been much explored in organometallic reactions. It was only recently that gallium metal has been used in Barbier reactions,[6] Reformatsky reactions.[7] Gallium compounds are also scarcely used for

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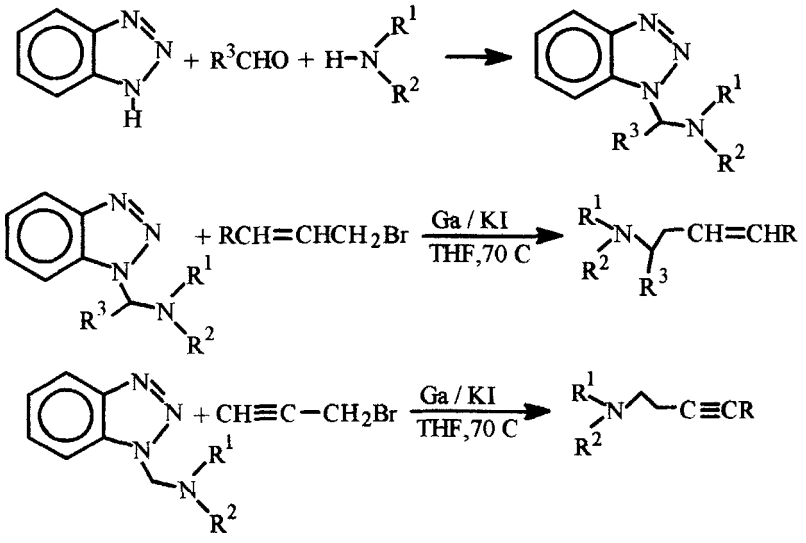
synthetic purposes. The only recent entry is the alkynylation of aldehydes mediated by GaI_3.[8]

Benzotriazole methodology has already come a long way, but in the last decade benzotriazole has taken its place as one of the most useful synthetic auxiliary groups available to the preparative chemist.[9] Many types of compounds have been synthesized via benzotriazole auxiliary.[10] The most direct and easiest preparation of compounds by benzotriazole methodology is amines. Here we wish to report that mediated by metallic gallium, 1-(α -aminoalkyl) benzotriazole reacted with allylic and propargyl bromide to give homoallylic and homopropargyl amines in moderate to good yields:



Homoallylic amines are valuable precursors for a number of α -substituted alkylamines.[11] They are accessible through allylation and propargylation of imines, but it is easier and simpler to prepare the 1-(α -aminoalkyl) benzotriazole than imines. Compared to the bismuth chloride-aluminum promoted alkylations,[12] the contents of N-(2, 3-butadienyl) amines are low (entry 6, 7, 8). We provide here a novel alternative route to homoallylic and homopropargyl amines with the

Table Products and Yields

Entry	Product	React. Time(h)	Yield[a] (%)
1	$PhNHCH_2CH_2CH{=}CH_2$	6	85
2	$o\text{-}CH_3C_6H_4NHCH_2CH_2CH{=}CH_2$	5	86
3	$p\text{-}CH_3C_6H_4NHCH_2CH_2CH{=}CH_2$	5	72
4	$m\text{-}ClC_6H_4NHCH_2CH_2CH{=}CH_2$	6	81
5	$o\text{-}CH_3C_6H_4NHCHCH_2CH{=}CH_2$ (CH$_3$ on CH)	6	75
6	$PhN(CH_3)CH_2CH_2C{\equiv}CH$ $PhN(CH_3)CH_2CH{=}C{=}CH_2$	5	78[b] (100) (0)
7	$Ph_2NCH_2CH_2C{\equiv}CH$ $Ph_2NCH_2CH{=}C{=}CH_2$	5	65[b] (76) (24)
8	$PhNHCH_2CH_2C{\equiv}CH$ $PhNHCH_2CH{=}C{=}CH_2$	6	80[b] (92) (8)

a. Isolated yield. b. Total yield.

advantage of readily available starting materials, straightforward and simple synthetic procedures, mild reaction conditions and good yields of products.

EXPERIMENTAL

^{1}H-NMR spectra were recorded in CCl_4 on JEOL PMX 60si spectrometer using TMS as internal standard. IR spectra were obtained on a PE 683 spectrometer (neat). 1-(α -Aminoalkyl)benzotriazole is prepared according to reference 13. The reaction were performed in a Schlenk type glass apparatus and under a nitrogen atmosphere.

General procedure: In a 50mL three-necked round bottomed flask are placed 1.5 mmol gallium powder (2mmol, 0.14g), KI (0.08g), 1-(α -aminoalkyl) benzotriazole (3mmol). After purged with N_2, allylic bromide (4mmol, 0.49g) and THF (20mL) were added. The mixture is stirred under nitrogen at 70℃ for a given time, until the gallium powder are almost consumed. The mixture is

extracted with ether twice (30mL × 2) after treated with brine (10mL). Organic layer is worked as usual and the solvents are evaporated in vacuum. The product is separated from residue through preparative TLC (silica gel) with cyclohexane/ ethyl acetate (13/1) as eluent.

N-(3-Butenyl)aniline (1): oil; ^{1}H NMR: 7.20-6.94(m, 2H), 6.70-6.39(m, 3H), 6.16-5.51(m, 1H), 5.19-4.94(m, 2H), 3.43(s, 1H), 3.14(t, 2H, J=6.7Hz), 2.31(q, 2H, J=6.7Hz); IR: 3435, 3100, 3075, 3040, 3000, 2940, 2870, 1850, 1652, 1615, 1596, 1515, 1480, 1440, 1325, 1270, 1180, 1160, 1100, 1075, 995, 915, 870, 745, 690cm^{-1}

N-(3-Butenyl)-o-methylaniline (2): oil; ^{1}H NMR: 7.16-6.87(m, 2H), 6.65-6.42(m, 2H), 6.18-5.52(m, 1H), 5.23-4.96(m, 2H), 3.20(s, 1H, NH), 3.17(t, 2H, J=6.7Hz), 2.38(q, 2H, J=6.7Hz), 2.04(s, 3H); IR: 3450, 3090, 3030, 2990, 2925, 2860, 1850, 1648, 1615, 1595, 1520, 1476, 1450, 1380, 1318, 1265, 1050, 990, 910, 740, 710.

N-(3-Butenyl)-p-methylaniline[12] (3): oil; ^{1}H NMR: 6.94-6.29(m, 4H), 6.12-5.47(m, 1H), 5.17-4.89(m, 2H), 3.29(s, 1H, NH), 3.07(t, 2H, J=7Hz), 2.34(t, 2H, J=7Hz), 2.20(s, 3H); IR: 3435, 3100, 3040, 3000, 2940, 2880, 1840, 1650, 1630, 1596, 1530, 1490, 1325, 1310, 1266, 1188, 1130, 995, 915, 805, 700.

N-(3-Butenyl)-m-chloroaniline (4): oil; ^{1}H NMR: 7.13-6.87(t, 1H), 6.65-6.26(m, 3H), 6.14-5.47(m, 1H), 5.20-4.89(m, 2H), 5.57(s, 1H, NH), 3.09(t, 2H, J=6.7Hz), 2.31(t, 2H, J=6.7Hz); IR: 3440, 3095, 3040, 3015, 2990, 2930, 2860, 1850, 1648, 1610, 1510, 1490, 1440, 1425, 1330, 1280, 1165, 1085, 985, 915, 830, 755, 675cm.

N-(1-Methyl-3-butenyl)-o-methylaniline (5): oil; ^{1}H NMR: 7.15-6.87(m, 2H), 6.64-6.43(m, 2H), 6.18-5.50(m, 1H), 5.16-4.89(m, 2H), 3.47(six peaks with J=6Hz, 2H), 3.34(s, 1H, NH), 2.29(t, 2H, J=6Hz), 2.06(s, 3H), 1.22(d, 3H, J=6Hz); IR: 3450, 3090, 3030, 2980, 2935, 2880, 1850, 1650, 1615, 1590, 1520, 1510, 1485, 1450, 1380, 1320, 1260, 1160, 1050, 990, 910, 740, 710.

N-(3-Butynyl)-N-methylaniline/N-(2,3-Butadienyl)-N-methylaniline[12] (6): oil;

100/0; ^{1}H NMR: 1.89(t, J=2.8Hz, 1H), 2.37(dt, J=7, 2.8Hz, 2H), 2.97(s, 3H), 3.54(t, J=7Hz, 2H), 6.47-6.80(m, 3H), 6.99-7.26(m, 2H); IR: 3340, 2125, 630.

(3-Butynyl)diphenylamine/(2,3-Butadienyl)diphenylamine[12] (7): oil; inseparable mixture, relative content is 76/24 according to NMR; (3-Butynyl)diphenylamine: ^{1}H NMR; 1.86(t, J=2.8Hz, 1H), 2.51(dt, J=7.6, 2.8Hz, 2H), 3.87(s, 1H), 3.91(t, J=7.6Hz, 2H), 6.74-7.36(m, 10H); IR: 3330, 2125, 1249, 635; (2,3-Butadienyl)diphenylamine: ^{1}H NMR; 4.23-4.43(m, 2H), 4.59-4.81(m, 2H), 5.04-5.43(quint, J=6Hz 1H), 6.74-7.36(m, 10H); IR: 3330, 1970, 1370, 1060, 841.

N-(3-Butynyl)aniline/N-(2,3-Butadienyl)aniline (8): oil; inseparable mixture, relative content is 92/8 according to NMR; N-(3-Butynyl)aniline: ^{1}H NMR: 1.94(t, J=2.8Hz, 1H), 2.38(dt, J=6.6, 2.8, 2H), 3.25(t, J=6.6Hz, 2H), 3.66(m, 1H), 6.42-6.73(m, 3H), 6.97-7.23(m, 2H); IR: 3435, 3320, 2120, 1266, 635. N-(2,3-Butadienyl)aniline: ^{1}H NMR: 3.56-3.78(m, 2H), 4.65-4.93(m, 2H), 5.07-5.45(quint, J=6Hz, 1H), 6.42-6.73(m, 3H), 6.97-7.23(m, 2H); IR: 3435, 1975, 1373, 870.

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