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Synthesis of *N*-allylanilines by the reductive allylboration of aromatic nitro compounds

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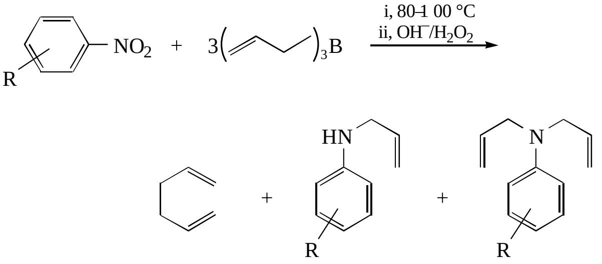
A new method for the synthesis of *N*-allylanilines and *N*,*N*-diallylanilines was developed on the basis of triallylborane reactions with aromatic compounds.

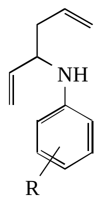
Nitroarenes react with arylmagnesium[1–3] and allylmagnesium[3,4] halides to form products of the 1,2-addition at the N=O bond, which afford N,N-disubstituted hydroxylamines,[1,3] secondary amines[3,4] or nitrones[4] depending on conditions of the subsequent treatment. Nitroarenes were alkylated at the ring under the action of aliphatic RMgX.[3,5,6] Aniline, PhNHEt, $PhNEt_2$, 2- and $4\text{-}EtC_6H_4NH_2$, *etc*., were identified among the products of the reaction between $PhNO_2$ and Et_3Al.[7]

We examined the transformations of nitroaromatic compounds (nitrobenzene, *p*-chloronitrobenzene, *p*-nitrobiphenyl and *o*-nitrobiphenyl) under the action of triallylborane. The reactions were performed by adding a nitroarene to triallylborane (1:3) heated to 80–100 °C (in a toluene or carbon tetrachloride solvent or without a solvent) followed by the treatment of the reaction mixture with an alkaline hydrogen peroxide solution or triethanolamine. We found that diallyl **1** and corresponding *N*-allylanilines **2a**–**d** and *N*,*N*-diallylanilines **3a**–**d**, which can be easily separated by chromatography or by distillation, were the main reaction products.



1, 30–35%	**2a**–**d**	**3a**–**d**
a R = H	60%	10%
b R = *p*-Cl	63%	5.5%
c R = *p*-Ph	60%	9.5%
d R = *o*-Ph	46%	15%

In addition to **1**–**3**, allyl alcohol (< 5%) and diene compounds **4** and **5** (< 5% in total) were identified in the reaction products. The latter resulted from the allylation of amine **2** at the side chain and the aromatic ring, respectively.



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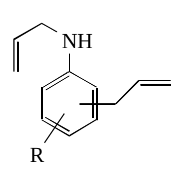

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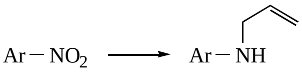
Thus, triallylborane reacts with nitroarenes by 1,2-addition to the nitro group, and this reaction is the first example of the allylboration of compounds containing N=O bonds. The subsequent reduction of the adduct with an excess of triallylborane resulted in *N*-allylanilines **2**. The redox reaction was accompanied by the generation of allyl radicals, which recombine to form diallyl **1**, and radical substitution resulted in minor allylation products such as 3-(hexa-1,5-dienyl)aniline **4**.

Although the reductive allylboration of aromatic nitro compounds is a complex reaction, this reaction is a simple new route to convert a nitro group in aromatic compounds into an *N*-allylamine group.



The structures of the prepared compounds were confirmed by elemental analysis, mass spectrometry, and ^1H and ^{13}C NMR spectroscopy. The chemical shifts δ in ^1H NMR spectra were measured with reference to the signals of residual chloroform.[†]

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[†] **2a**: 60% yield; n_D^{20} 1.5634 (lit.,[8] 1.5636). ^1H NMR (200 MHz, $CDCl_3$) δ: 3.90 (br. s, 1H, NH), 3.95 (d, 2H, CH_2N, *J* 5.8 Hz), 5.30–5.55 (m, 2H, CH_2=, vinyl), 6.05–6.25 (m, 1H, CH=, vinyl), 6.80 (d, 2H, C^2H, Ph, *J* 7.8 Hz), 6.95 (t, 1H, C^4H, Ph, *J* 7.4 Hz), 7.35–7.45 (m, 2H, C^3H, Ph). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 147.9 (C^1, Ph), 135.3 (CH=, vinyl), 129.0 (C^3, Ph), 117.25 (C^4, Ph), 115.9 (CH_2=, vinyl), 112.75 (C^2, Ph) 46.25 (CH_2N). MS, *m*/*z*: 133 (M^+).

2b: 63% yield; n_D^{20} 1.5784. ^1H NMR (200 MHz, $CDCl_3$) δ: 4.00–4.10 (m, 3H, CH_2N, NH), 5.40–5.70 (m, 2H, CH_2=, vinyl), 6.15–6.35 (m, 1H, CH=, vinyl), 6.85 (d, 2H, C^2H, Ph, *J* 8.8 Hz), 7.45 (d, 2H, C^3H, Ph, *J* 8.8 Hz). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 146.5 (C^1, Ph), 134.9 (CH=, vinyl), 128.9 (C^3, Ph), 121.8 (C^4, Ph), 116.3 (CH_2=, vinyl), 113.9 (C^2, Ph), 46.4 (CH^2N). MS, *m*/*z*: 167 (M^+). Found (%): C, 64.66; H, 6.10; N, 8.25; Cl, 21.09. Calc. for $C_9H_{10}NCl$ (%): C, 64.44; H, 6.01; N, 8.35; Cl, 21.11.

2c: 60% yield; mp 63–64 °C. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.70–3.85 (m, 3H, CH_2N, NH), 5.10–5.35 (m, 2H, CH_2=, vinyl), 5.85–6.05 (m, 1H, CH=, vinyl), 6.65 (d, 2H, C^2H, C_6H_4, *J* 7.7 Hz), 7.15–7.55 (m, 5H, C_6H_5, 2H, C^3H, C_6H_4). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 147.4 (C^1, C_6H_4), 141.4 (C^1, C_6H_5), 135.2 (CH=, vinyl), 130.25 (C^4, C_6H_4) 128.55 (C^3, C_6H_4), 127.8 (C^3, C_6H_5), 126.2 (C^2, C_6H_5), 125.95 (C^4, C_6H_5), 116.2 (CH_2=, vinyl), 113.1 (C^2, C_6H_4), 46.4 (CH_2N). MS, *m*/*z*: 209 (M^+). Found (%): C, 85.90; H, 7.46; N, 6.64. Calc. for $C_{15}H_{15}N$ (%): C, 86.08; H, 7.22; N, 6.69.

2d: 46% yield; n_D^{20} 1.6150. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.90 (d, 2H, CH_2N, *J* 5.4 Hz), 4.25 (br. s, 1H, NH), 5.20–5.40 (m, 2H, CH_2=, vinyl), 5.95–6.10 (m, 1H, CH=, vinyl), 6.80–7.60 (m, 9H, Ar). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 144.7 (C^1, C_6H_4), 139.4 (C^1, C_6H_5), 135.3 (CH=, vinyl), 130.1 (CH, Ar) 129.3 (CH, Ar), 128.8 (CH, Ar), 128.55 (CH, Ar), 127.6 (C^2, C_6H_4), 127.1 (CH, Ar), 117.0 (CH, Ar), 115.7 (CH_2=, vinyl), 110.7 (CH, Ar), 46.2 (CH_2N). MS, *m*/*z*: 209 (M^+). Found (%): C, 86.28; H, 7.26; N, 6.84. Calc. for $C_{15}H_{15}N$ (%): C, 86.08; H, 7.22; N, 6.69.

3a: 10% yield; n_D^{20} 1.5548 (lit.,[8] 1.5538). ^1H NMR (200 MHz, $CDCl_3$) δ: 4.05 (d, 4H, CH_2N, *J* 4.7 Hz), 5.25–5.35 (m, 4H, CH_2=, vinyl), 5.85–6.05 (m, 2H, CH=, vinyl), 6.70–6.85 (m, 3H, C^2H, C^4H, Ph), 7.25–7.35 (m, 2H, C^3H, Ph). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 148.6 (C^1, Ph), 133.9 (CH=, vinyl), 129.0 (C^3, Ph), 116.2 (C^4, Ph), 115.85 (CH_2=, vinyl), 112.2 (C^2, Ph) 52.6 (CH_2N). MS, *m*/*z*: 173 (M^+).

3b: 5.5% yield; n_D^{20} 1.5695. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.75–3.85 (m, 4H, CH_2N), 5.05–5.15 (m, 4H, CH_2=, vinyl), 5.55–5.85 (m, 2H, CH=, vinyl), 6.55 (d, 2H, C^2H, Ph, *J* 9.1 Hz), 7.05 (d, 2H, C^3H, Ph, *J* 9.1 Hz). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 147.2 (C^1, Ph), 133.5 (CH=, vinyl), 128.8 (C^3, Ph), 121.0 (C^4, Ph), 116.1 (CH_2=, vinyl), 113.4 (C^2, Ph), 52.9 (CH_2N). MS, *m*/*z*: 207 (M^+).

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3c: 9.5% yield; n_D^{20} 1.5834. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.95 (d, 4H, CH_2N, *J* 4.9 Hz), 5.00–5.25 (m, 4H, CH_2=, vinyl), 5.65–5.90 (m, 2H, CH=, vinyl), 6.75 (d, 2H, C^{2}H, C_6H_4, *J* 9.1 Hz), 7.05–7.55 (m, 7H, Ar). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 147.8 (C^1, C_6H_4), 141.2 (C^1, C_6H_5), 133.8 (CH=, vinyl), 130.2 (C^4, C_6H_4) 128.6 (C^3, C_6H_4), 127.65 (C^3, C_6H_5), 126.15 (C^2, C_6H_5), 125.9 (C^4, C_6H_5), 116.0 (CH_2=, vinyl), 112.45 (C^2, C_6H_4), 52.7 (CH_2N). MS, *m*/*z*: 249 (M$^+$).

3d: 15% yield; n_D^{20} 1.5842. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.55 (d, 4H, CH_2N, *J* 6.7 Hz), 5.10–5.20 (m, 4H, CH_2=, vinyl), 5.55–5.85 (m, 2H, CH=, vinyl), 7.05–7.75 (m, 9H, Ar). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ: 148.55 (C^1, C_6H_4), 141.5 (C, Ar), 136.0 (C, Ar), 135.0 (CH=, vinyl), 131.5 (CH, Ar), 129.0 (CH, Ar), 128.15 (CH, Ar), 127.6 (CH, Ar), 126.55 (CH, Ar), 122.35 (CH, Ar), 121.15 (CH, Ar), 117.1 (CH_2=, vinyl), 54.7 (CH_2N). MS, *m*/*z*: 249 (M$^+$).