Allylboration of nitrosobenzene

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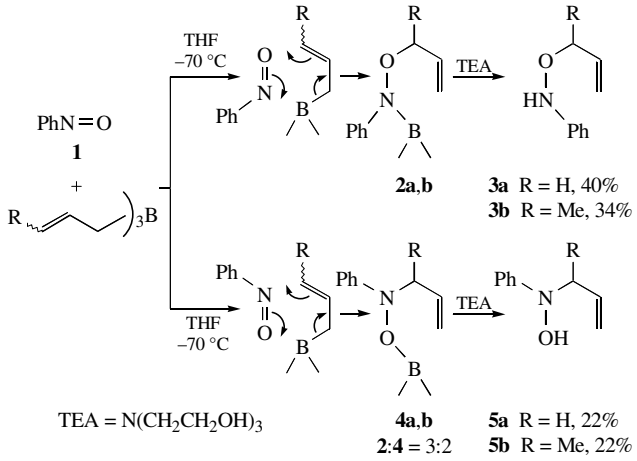
The allylboration of nitrosobenzene at –70 °C resulted in the formation of *N*- and *O*-allyl derivatives of *N*-phenylhydrazine, which were reduced with the second allylborane molecule to *N*-allylaniline above 100 °C.

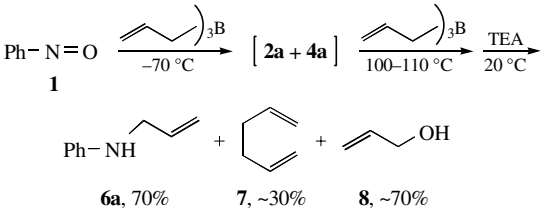
The heating of nitrosoarenes with trialkylboranes afforded corresponding anilines in low yields; the products of reductive alkylation were not detected.[1–3] The reactions of nitroaromatic substrates with allylboranes occurred at 80–100 °C and resulted in substituted *N*-allylanilines and *N*,*N*-diallylanilines.[4] The allylboration of nitroso compounds was not studied previously.

We found that nitrosobenzene **1** reacts with triallylborane and tricrotylborane at –70 °C to form two products of 1,2-addition at the N=O bond **2** and **4** in a ratio of 3:2 (according to NMR data). The deboration of them afforded O- and N-allylated phenylhydroxylamines **3** and **5**, respectively.† Thus, we detected the initially formed allylboration products in contrast to analogous reactions of triallylborane with nitro compounds.[4] In this case, it is surprising that predominant reaction product **2a** results from the addition of an allyl group and a boron atom at the oxygen and nitrogen atoms of the N=O bond, respectively. The low regioselectivity of nitroso group allylboration is of particular interest. It is well known that all of the previously studied reactions of allylborane addition to compounds with polarised multiple bonds are completely regiospecific with no exception.

Tricrotylborane with nitrosobenzene gives compounds **3b** and **5b**, which contain α-methylallyl groups. Thus, the reductive allylboration of an aromatic nitroso group occurred completely with the allyl rearrangement *via* a six-membered transition state (as in all other allylboration reactions). At the same time, the reasons for the low regioselectivity of this reaction remain unclear.



O-Allyl- and *N*-allyl-*N*-phenylhydroxylamine derivatives **2a** and **4a** react with the second mole of triallylborane (100–110 °C) with the formation of *N*-allylaniline **6a**, diallyl **7** and allyl alcohol **8**.



The reduction of intermediate products **2** and **4** was found to occur *via* completely different mechanisms.

The action of triallylborane on compound **5a** (1:1) resulted in practically pure derivative **4a**. The heating of the latter with an additional mole of triallylborane and the subsequent deboration resulted in *N*-allylaniline **6a** and diallyl **7**. Compound **5b** reacted analogously to give *N*-(1-methylallyl)aniline **6b** and diallyl **7**. In this case, the redox process associated with N–O bond cleavage was accompanied by the generation of allyl radicals, the recombination of which afforded diallyl. The formation of radical combination products such as biphenyl in the reaction of arylmagnesium compounds with hydroxylamine derivatives is well known.[5]

At the same time, the formation of *N*-allylaniline from compound **3a** formally is the replacement of the *O*-allyl group by an allyl group. It is interesting in the test reaction that the entering allyl group retains its configuration; that is, the reaction of *O*-allyl derivatives with allylboranes occurs with no allyl rearrangement. This was found in the action of tricrotylborane on *O*-allyl derivatives **2**.

A few allylborane reactions that occur by the direct cleavage of the boron–carbon bond (with no allyl rearrangement) are

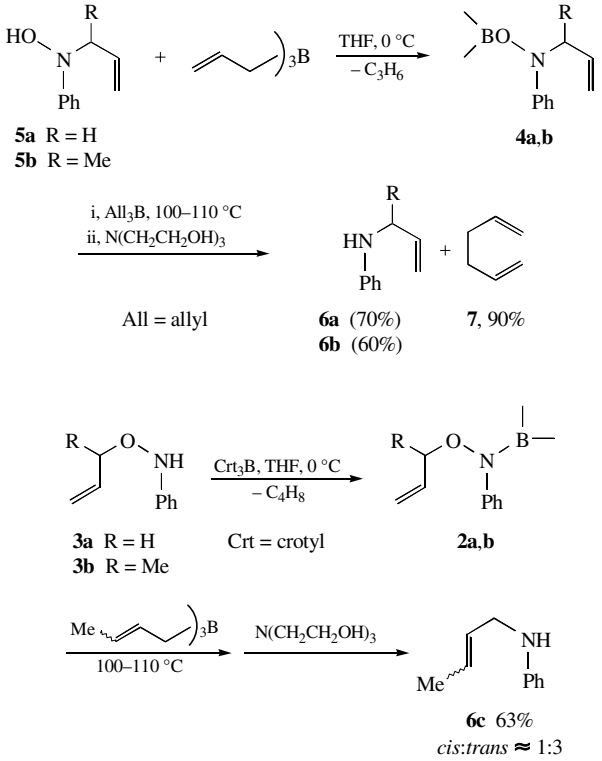
† *General procedure for nitrosobenzene allylboration. Synthesis of* N- *and* O-*allyl derivatives of* N-*phenylhydroxylamine* **3** *and* **5**. A solution of 50 mmol of nitrosobenzene in 150 cm^3 of THF was added dropwise to a solution of 50 mmol R_3B (R = All, Crt) in 75 cm^3 of THF at –65 °C with continuously stirring. The mixture was heated to 20 °C and stirred for 2 h. After deboration with triethanolamine (46.6 mmol in 20 cm^3 of THF), the mixture of products **3** and **5** was separated by column chromatography on SiO_2 (hexane–diethyl ether, 10:1).

O-*Allyl*-N-*phenylhydroxylamine* **3a**: yellow oil, 2.8 g (40%) yield, bp 49–52 °C (0.01 Torr). n_D^{18} = 1.5395. ^{1}H NMR ($CDCl_3$) δ: 4.5 (d, 2H, OCH_2, *J* 6.2 Hz), 5.3–5.5 (m, 2H, $=CH_2$), 5.9–6.25 (m, 1H, CH=), 6.9 (d, 2H, *o*-H, *J* 8.8 Hz), 7.05 (m, 1H, *p*-H), 7.2 (br. s, 1H, NH), 7.25 (m, 2H, *m*-H). ^{13}C NMR ($CDCl_3$) δ: 75.8 (O–C), 114.2 (*o*-C), 118.6 (*p*-C), 121.7 ($=CH_2$), 128.8 (*m*-C), 133.4 (CH=), 148.35 (*i*-C). MS, *m*/*z*: 149 $[M]^+$. Found (%): C, 72.44; H, 7.37. Calc. for $C_9H_{11}NO$ (%): C, 72.45; H, 7.43.

N-*Allyl*-N-*phenylhydroxylamine* **5a**: yellow oil, 1.54 g (22%) yield. ^{1}H NMR ($CDCl_3$) δ: 4.05 (d, 2H, NCH_2, *J* 5.4 Hz), 5.3–5.5 (m, 2H, $=CH_2$), 5.9–6.2 (m, 1H, CH=), 6.9 (br. s, OH), 7.05 (m, 2H, *m*-H), 7.2 (d, 2H, *o*-H, *J* 7.7 Hz), 7.35 (m, 1H, *p*-H). ^{13}C NMR ($CDCl_3$) δ: 62.4 (N–C), 116.9 (*o*-C), 118.9 ($=CH_2$), 122.4 (*p*-C), 128.6 (*m*-C), 133.1 (CH=), 152.1 (*i*-C). MS, *m*/*z*: 149 $[M]^+$. Found (%): C, 72.48; H, 7.38. Calc. for $C_9H_{11}NO$ (%): C, 72.45; H, 7.43.

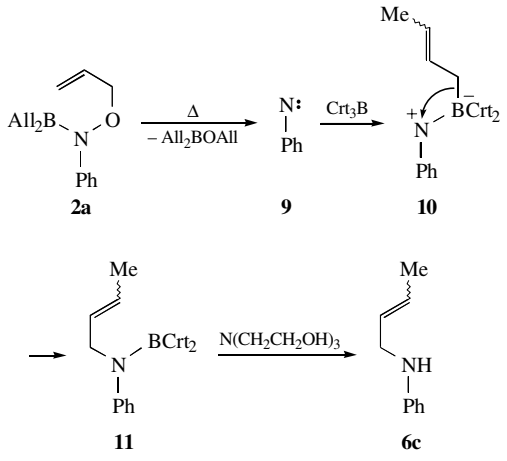
O-*(1-Methylprop-2-en-1-yl)*-N-*phenylhydroxylamine* **3b**: 2.6 g (34%) yield, bp 82–84 °C (0.01 Torr). n_D^{18} = 1.5275. ^{1}H NMR ($CDCl_3$) δ: 1.45 (d, 2H, Me, *J* 7.2 Hz), 4.4 (m, 1H, OCH), 5.25–5.4 (m, 2H, $=CH_2$), 5.9–6.1 (m, 1H, CH=), 6.9 (s, NH) 7.0–7.1 (m, 3H, *o*-H, *p*-H), 7.3–7.4 (m, 2H, *m*-H). ^{13}C NMR ($CDCl_3$) δ: 19.4 (Me), 80.6 (O–C), 114.4 (*o*-C), 117.4 (*p*-C), 121.85 ($=CH_2$), 129.1 (*m*-C), 139.1 (CH=), 148.8 (*i*-C). MS, *m*/*z*: 163 $[M]^+$. Found (%): C, 73.87; H, 8.23. Calc. for $C_{10}H_{13}NO$ (%): C, 73.58; H, 8.03.

N-*(1-Methylprop-2-en-1-yl)*-N-*phenylhydroxylamine* **5b**: 1.7 g (22%) yield, bp 92–95 °C (0.01 Torr). n_D^{18} = 1.5422. ^{1}H NMR ($CDCl_3$) δ: 1.35 (d, 3H, Me, *J* 16.4 Hz), 4.1–4.25 (m, 1H, NCH), 5.05–5.2 (m, 2H, $=CH_2$), 6.0–6.1 (m, 1H, CH=), 7.0 (br. s, 1H, OH), 7.4–7.6 (m, 5H, aromatic protons). ^{13}C NMR ($CDCl_3$) δ: 15.7 (Me), 65.0 (N–C), 116.7 ($=CH_2$), 118.5 (*o*-C), 122.8 (*p*-C), 128.6 (*m*-C), 138.0 (CH=), 151.5 (*i*-C). MS, *m*/*z*: 163 $[M]^+$. Found (%): C, 73.55; H, 8.05. Calc. for $C_{10}H_{13}NO$ (%): C, 73.58; H, 8.03.



known. They take place by the 1,2-migration of an allyl radical to an electron-deficient centre neighbouring to the boron atom.[6]

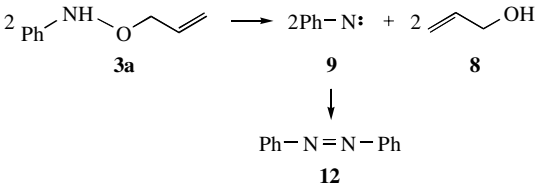
We believe that nitrene **9** is generated from *O*-allyl derivative **2a**. This nitrene is bound to tricrotylborane to form betaine **10**. The 1,2-anionotropic rearrangement in the letter, which is typical of the chemistry of boron,[6] leads to aminoborane **11**, the protolysis of which results in crotylaniline **6c**.‡



‡ cis-N-*(2-But-1-enyl)aniline* **6c**-*cis*. ^{1}H NMR ($CDCl_3$) δ: 1.85 (d, 3H, Me, *J* 6.7 Hz), 3.7 (br. s, NH), 3.9 (d, 2H, NCH_2, *J* 7.3 Hz), 5.6–5.9 (m, 2H, CH=CH), 6.75 (d, 2H, *o*-C, *J* 13.3 Hz), 6.8–6.9 (m, 1H, *p*-C), 7.2–7.4 (m, 2H, *m*-C). ^{13}C NMR ($CDCl_3$) δ: 12.9 (Me), 40.7 (N–C), 112.8 (*o*-C), 117.1 (*p*-C), 127.6, 128.0 (CH=), 129.0 (*m*-C), 165.0 (*i*-C).

trans-N-*(2-But-1-enyl)aniline* **6c**-*trans*. ^{1}H NMR ($CDCl_3$) δ: 1.85 (d, 3H, Me, *J* 6.7 Hz), 3.75 (d, 2H, NCH_2, *J* 8.0 Hz), 5.6–5.9 (m, 2H, CH=CH), 6.75 (d, 2H, *o*-C, *J* 13.3 Hz), 6.8–6.9 (m, 1H, *p*-C), 7.2–7.4 (m, 2H, *m*-C). ^{13}C NMR ($CDCl_3$) δ: 17.6 (Me), 45.8 (N–C), 112.8 (*o*-C), 117.2 (*p*-C), 127.0 (CH=), 127.6 (*m*-C), 128.0 (=CH), 148.1 (*i*-C).

Note that *O*-allyl-*N*-phenylhydroxylamine **3a**, which is a product of the first step of nitrosobenzene allylboration, is spontaneously decomposed in solution at room temperature, and this decomposition is accelerated by light. Azobenzene **12** and allyl alcohol **8** are the decomposition products of compound **3a**. In this case, the formation of phenylnitrene **9** is also highly probable. α-Methylallyl derivative **3b** behaves similarly in storage.



Published data indicate that nitrenes can be generated from hydroxylamine derivatives.[7,8] Thus, it was found recently that *N*-lithium derivatives of *N*-benzyl-*O*-(2-alkenyl)hydroxylamine decompose to form benzylnitrene and the *O*-lithium derivative of the corresponding allyl alcohol.[8]

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References

1 T. Okushi, O. Manabe, H. Hiyama and Z. Yoshida, *Koguo Kagaku Zasshi*, 1969, **72**, 1665 (*Chem. Abstr.*, 1970, **72**, 11797c).
2 Z. Yoshida, T. Okushi, O. Manabe and H. Hiyama, *Tetrahedron Lett.*, 1965, 753.
3 M. Inatome and L. P. Kuhn, in *Boron-Nitrogen Chemistry. Advances in Chemistry Series*, ed. R. F. Gould, 1964, vol. 42, p. 183.
4 (*a*) Yu. N. Bubnov, D. G. Pershin, A. V. Ignatenko and M. E. Gurskii, *Mendeleev Commun.*, 2000, 108; (*b*) D. G. Pershin, Yu. N. Bubnov, M. E. Gurskii and A. V. Ignatenko, in *Contemporary Boron Chemistry*, eds. M. Davidson, A. K. Hughes, T. V. Marder and K. Wade, Royal Society of Chemistry, Cambridge, 2000, p. 450.
5 (*a*) H. Gilman and R. McCracken. *J. Am. Chem. Soc.*, 1927, **49**, 1052; (*b*) D. N. Kursanov and P. A. Solodkov, *Zh. Obshch. Khim.*, 1935, **5**, 1487 (in Russian); (*c*) Y. Yost, H. R. Gutman and C. C. Muskoplat, *J. Chem. Soc. (C)*, 1971, 2119.
6 B. M. Mikhailov and Yu. N. Bubnov, *Organoborane Compounds in Organic Synthesis*, Harwood Acad. Sci. Pbs., London, 1984.
7 R. Appel and O. Buchner, *Angew. Chem., Int. Ed. Engl.*, 1962, **1**, 332.
8 T. Ishikawa, M. Kawakami, M. Fukui, A. Yamashita, J. Urano and S. Saito, *J. Am. Chem. Soc.*, 2001, **123**, 7734.

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