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Thermal *trans-cis*-isomerization of *trans*-2,6-diallyl-Δ^3-piperideine by the action of triallylborane

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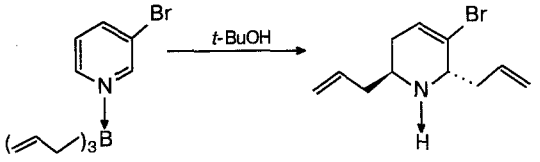
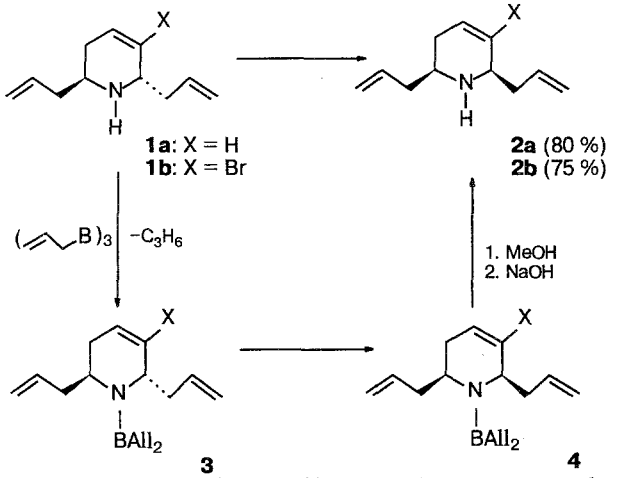
Interaction between the pyridine complex of triallylborane with alcohols (2—4 moles, 40—100 °C) affords *trans*-2,6-diallyl-Δ^3-piperideine (*trans*-2,6-diallyl-1,2,5,6-tetrahydropyridine) (**1a**) in ~98 % yield.[1] In the course of a study of this new reaction, which we named reducing *trans*-diallylation of pyridines, *trans*-2,6-diallyl-3-bromo-1,2,5,6-tetrahydropyridine (**1b**) was obtained (83 %); the structure of its hydrocloride was determined by X-ray structural analysis.[2]



1b

trans-Isomers **1a**, **b** were transformed into the corresponding *cis*-2,6-diallylic derivatives in nearly quantative yield on heating with triallylborane (125—130 °C, 5—6 h).

It is possible that this occurs as a multistage process. Previously, as a result of the decomposition of one of the B—C bonds in triallylborane[3] and the elimination of propylene, aminoborane (**3**) was formed. It was transformed into the corresponding *cis*-derivative (**4**) on heating. Subsequent deboration of **4** with methanol



(0—20 °C) and NaOH (10 %, 1.2 eq.) led to *cis*-2,6-diallyl-1,2,5,6-tetrahydropyridine (**2a**) or its 3-bromo derivative (**2b**). Mixtures of the *trans*-isomers (1.5—2.0 % in **2a** and 6 % in **2b**) were easily separated by chromatography on SiO_2 (eluent — pentane). The yields of **2a** and **2b** were 80 % and 75 %, respectively.

The isomerization of **1a** to **2a** also occurs during heating with allyl(dipropyl)borane (140—150 °C, 5 h).

cis-2,6-Dipropylpiperidine (**5**) (90 %) was synthesized by hydrogenation of **1a** with Raney nickel in acetic acid (90 °C, 9 MPa H_2). This compound was trans-

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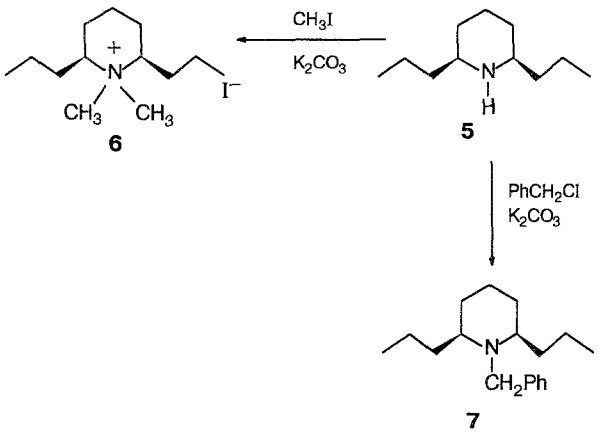
formed into the corresponding quarternary salt (**6**) (99 %) and the N-benzyl derivative (**7**) (70 %).



The H^1 NMR spectrum of salt **6** shows two singlets for nonequivalent methyl groups at 2.88 and 3.40 ppm. The enantiotopic protons of the benzylic group in the spectrum of compound **7** were present as a singlet at 3.65 ppm. These data unambiguously indicate the *cis*-orientation of the propyl groups in **5** and the allylic groups in **2a**, respectively.

Some parameters of the synthesized compounds are given below: b.p./°C (*p*, Torr), n_D^{20}, m.p./°C (for hydrochloride): **1a**, 53—54 (1), 1.4893, 177.5—178.5 (*cf.* ref. 1); **1b**, 85—86 (1), 1.5251, 165—166; **2a**, 52—53 (1), 1.4854, 225—226; **2b**, 98 (1.5), 1.5242, 162—162.5; **5**, 62 (1), 1.4531, 225—226; **6**, —, —, 132.5—143; **7**, 120 (1), 1.5132, —.

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Absolute configuration of somane

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Organophosphorus war gases (nerve gases), in particular, somane, exhibit the highest toxicity[1] and mutagenic activity.[2] Stereoisomers of somane (**1**) differ in their anticholinesterase action and acute toxicity by 10^4—10^5 and 10^2 times, respectively.[1] This is why knowledge of the absolute configuration of somane has become a primary concern in the rational search for antidotes,[1] especially since recently[3] the structure of the enzyme acetylcholinesterase, which is the basic target for **1**, has been carefully studied.

We have found that two series of signals for diastereomers are observed in the ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of a C_6D_6 solution of somane in the same ratio (1.2 : 1) as in the chromatographic analysis[1] (Fig. 1). In the ^1H NMR spectrum in the presence of the chiral shift reagent Eu(tfc)$_3$, signals of all four stereoisomers can be resolved; in this case, the four paired signals of the *t*-Bu group differing in intensity reproduce the features of the chromatogram on a chiral phase[4] (Fig. 1).

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