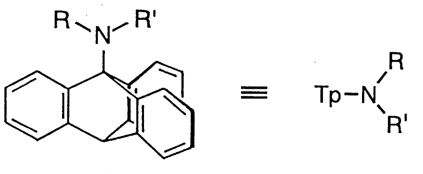
Structure and Stereodynamics of *N*-9-Triptycyl-*O*-phenylhydroxylamine, an Unusual Product by the Reaction of 9-Nitrosotriptycene and Phenyllithium

Gaku Yamamoto,* Kyoko Kuwahara, and Katsuya Inoue
Department of Chemistry, School of Science, Kitasato University, Kitasato, Sagamihara, Kanagawa 228

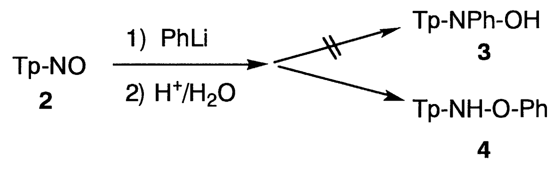
(Received February 7, 1995)

Reaction of 9-nitrosotriptycene with phenyllithium gave *N*-9-triptycyl-*O*-phenylhydroxylamine (TpNHOPh). The free energy barrier to rotation about the Tp-N bond is 10.9 kcal mol^{-1} and that to the N-O topomerization is higher than this.

We have recently been interested in the stereodynamics of *N*-substituted 9-triptycylamine derivatives **1**.[1] Synthesis of these compounds, especially of *N*-aryl-9-triptycylamines is rather difficult and development of general synthetic methods has been desired. As one of the procedures for preparing *N*-aryl-9-triptycylamines, we thought of the reduction of *N*-aryl-*N*-9-triptycylhydroxylamines, which would be prepared by reaction of 9-nitrosotriptycene (**2**) with aryllithium reagents; reactions of nitrosoalkanes with aryllithiums are known to afford *N*-alkyl-*N*-arylhydroxylamines. Therefore, we tried the reaction of **2** with phenyllithium expecting the formation of *N*-phenyl-*N*-9-triptycylhydroxylamine (**3**) (Scheme 1).



1: R=alkyl, aryl; R'=H, alkyl



Scheme 1.

Treatment of **2**[2] with phenyllithium at 0 °C followed by usual work-up and preparative TLC afforded colorless crystals in ca. 10% yield as a single isolable product. Elemental analysis of the product was satisfactory for the composition of **3** and ^{1}H and ^{13}C NMR spectral data also seemed consistent with **3**. However, a weak and narrow absorption at 3250 cm^{-1} in the IR spectrum was incompatible with O-H but rather pointed to the presence of N-H. These findings thus suggested that *N*-9-triptycyl-*O*-phenylhydroxylamine (**4**) was formed rather than **3**. Finally the X-ray crystallographic analysis unambiguously showed that the product was **4** (Figure 1).[3,4]

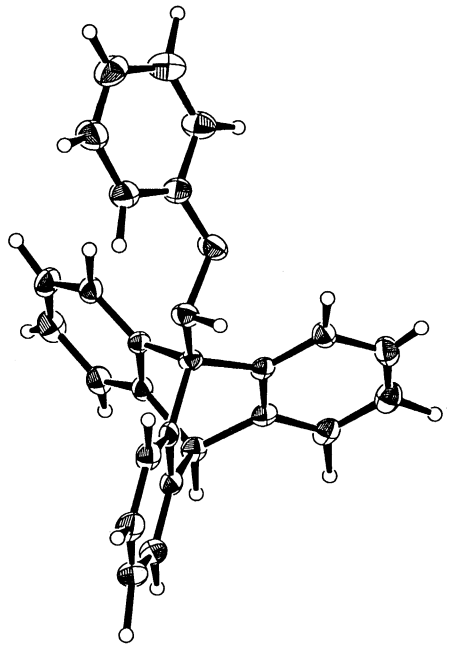
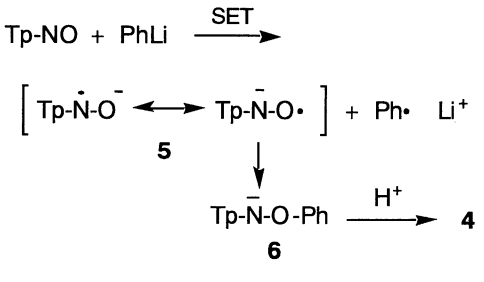


Figure 1. Perspective drawing of compound **4**.

A mechanism involving single electron transfer (SET) may tentatively be assumed for the formation of **4** although no firm experimental evidence is present (Scheme 2). The radical anion **5** formed by SET would combine with phenyl radical at the oxygen atom to afford **6** because the radical recombination at nitrogen is sterically highly hindered.

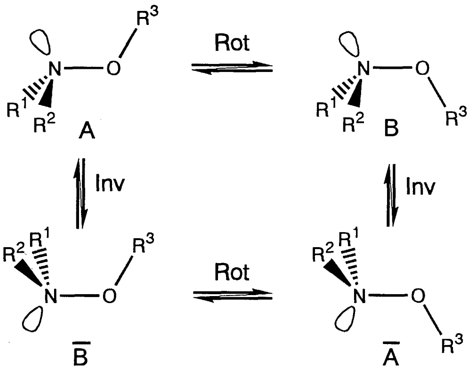


Scheme 2.

We got interested in this structurally remarkable compound and studied its stereochemistry in some detail.

Stereochemistry of hydroxylamines has been investigated both theoretically and experimentally.[5] Theoretical studies have revealed that there are two energy-minimum conformations (A and B in Scheme 3), in which the O-R bond is synperiplanar and antiperiplanar to the nitrogen lone pair, respectively, the former being more stable. Topomerization of the hydroxylamine moiety, *i.e.*, interconversion between the most stable conformation A and its enantiomer $\bar{A}$, takes place by sequential occurrence of inversion at nitrogen (Inv) and rotation about the N-O bond (Rot), the relative barrier heights of these two steps being dependent on the substituents.[5]

The X-ray molecular structure of **4** reveals that the Tp-N-O-Ph dihedral angle is 143.5° and this value is close to the one expected for conformation A (ca. 120°) in Scheme 3.



Scheme 3.

^{1}H and ^{13}C NMR spectral data at 25 °C indicated that rotation about the Tp-N bond was fast on the NMR time scale but afforded no information as for the rate of topomerization of the hydroxylamine moiety because of the lack of diastereotopic nuclei reflecting the topomerization. Upon lowering the temperature, the aromatic signals due to the Tp moiety broadened, split, and resharpened in both ^{1}H and ^{13}C spectra. At −87 °C the three benzene rings of the Tp group were mutually nonequivalent, as shown by the presence of 17 peaks for the Tp aromatic carbons, two carbons being accidentally isochronous. This situation is realized only when both of the Tp-N rotation and the N-O topomerization are slow on the NMR time scale. This means that the molecule is frozen into a conformation compatible with the X-ray structure given in Figure 1.[6]

The lineshapes of the Tp aromatic carbon signals at −44 ~ −70 °C could be analyzed in terms of one rate constant, *i.e.*, the one for the Tp-N rotation, affording 10.9±0.1 kcal mol^{-1} (1 cal = 4.184 J) for the free energy of activation of this process in this temperature range. This means that the Tp-N rotation is responsible for the observed lineshape change and the N-O topomerization has a higher energy barrier.[7] The $\Delta G^{\ddagger}$ value for the Tp-N rotation found in **4** may be compared with the value of 11.7 kcal mol^{-1} found in *N*-benzyl-*N*-methyl-9-triptycylamine (**1**: R=CH_2Ph, R'=CH_3)[1]: The eclipsing steric interaction between the *o*-benzeno moiety of the Tp group and the phenoxyl group at the transition state is mainly responsible for the energy barrier in **4**, while the one between the *o*-benzeno moiety and the benzyl group mainly constitutes the barrier in **1** as was discussed previously.[1]

In order to obtain further information about the stereodynamics of the N-O moiety, studies on such compounds as *N*-9-triptycyl-*O*-benzylhydroxylamine will be necessary. Further studies along this line are underway.

References and Notes

1 G. Yamamoto, H. Higuchi, M. Yonebayashi, and J. Ojima, *Chem. Lett.*, **1994**, 1911.

2 W. Theilacker and K.-H. Beyer, *Chem. Ber.*, **94**, 2968 (1961).

3 Physical and spectral data for compound **4**: mp 145–147 °C. Found: C, 86.34; H, 5.34; N, 3.92%. Calcd for $C_{26}H_{19}NO$: C, 86.40; H, 5.30; N, 3.88%. ^{1}H NMR ($CDCl_3$, 300.1 MHz) δ 5.387 (1H, s), 6.98–7.05 (6H, m), 7.094 (1H, m), 7.396 (3H, m), 7.439 (2H, m), 7.48–7.60 (6H, m). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 53.70 (1C, t), 71.14 (1C, q), 113.78 (2C, t), 121.61 (3C, t), 121.63 (1C, t) 123.34 (3C, t), 125.16 (3C, t), 125.49 (3C, t), 128.57 (2C, t), 143.85 (3C, q), 145.15 (3C, q), 160.56 (1C, q). IR (KBr) 3250 w, 1590 s, 1484 s, 1456 s, 1223 s, 744 s cm^{-1}.

4 X-ray crystallographic data for **4**: $C_{26}H_{19}NO$, FW=361.45, monoclinic, $P2_1/a$ (#14), a=13.92(1), b=8.16(1), c=16.56(1) Å, β=94.53(7)°, V=1876(3)Å^3, Z=4, D_{calc}=1.280 g cm^{-3}, R=0.068, R_w=0.046, 2262 unique reflections with $I > 3.0\sigma(I)$.

5 For reviews see: F. G. Riddell, *Tetrahedron*, **37**, 849 (1981); M. Raban and D. Kost, *Tetrahedron*, **40**, 3345 (1984); M. Raban and D. Kost, in "Acyclic Organonitrogen Stereodynamics," ed by J. B. Lambert and Y. Takeuchi, VCH Publishers, New York (1992), Chap. 2.

6 The ^{1}H and ^{13}C signals due to the phenyl group showed no temperature dependence, indicating that the O-Ph rotation is fast on the NMR time scale throughout the temperature range examined.

7 If the energy barrier to the N-O topomerization is lower than or similar to the one to the Tp-N rotation, the lineshape should depend on two kinds of rate constants, one for the N-O topomerization and one for the Tp-N rotation, which is not the case for **4**.