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Preliminary Communication

Reversible 1,3-Trimethylsilyl Migration Between Nitrogen and Oxygen in Trimethylsilylated N,O,O-Triphenylphosphoramidate

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Summary

Trimethylsilylated N,O,O-triphenylphosphoramidate has been synthesized and found by spectroscopic methods to exist as a mixture of 89% N- and 11% O-silylated isomers at 28° in α-bromonaphthalene solvent. Variable temperature ^{1}H NMR experiments with this mixture afforded the first thermodynamic and kinetic parameters associated with 1,3-trimethylsilyl migration between nitrogen and oxygen in a phosphoramidate system with $\Delta G_0 = 1.7$ kcal/mol (25°) and $\Delta G^{\neq} \sim 21\text{–}27$ kcal/mol.

Dynamical characteristics of intramolecular 1,3-trimethylsilyl migration between nitrogen and oxygen, and between nitrogen and sulfur, in trimethylsilyl derivatives of amides[1] and thioamides,[2] respectively, have been studied in considerable detail. Comparative kinetic parameters for tautomerization in the known[3] class of silylated phosphorus-containing analogs, viz. $\text{>P(O)-N<}^{\text{SiR}_3} \rightleftarrows \text{>P(OSiR}_3\text{)=N-}$, have not been heretofore available nor has this equilibrium been even detected; however, an estimation regarding the ground state enthalpy difference between such N- and O-silylated tautomers has been

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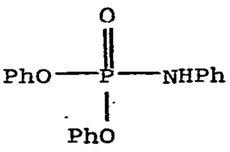
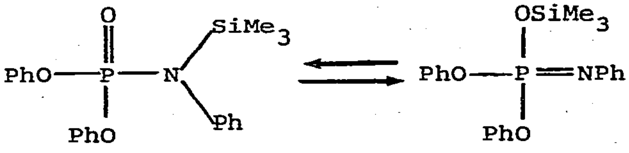
recently published.[4] We therefore wish to report the first quantitative experimental evidence regarding both the thermodynamics and kinetics of silyl group exchange between nitrogen and oxygen in a trimethylsilylated phosphoramidate.

Reaction of *N,O,O*-triphenylphosphoramidate[5] (I) with 50-fold molar excesses of chlorotrimethylsilane and triethylamine for 10 h. in refluxing anhydrous benzene gave, after removal of triethylamine hydrochloride and vacuum distillation, a 95% yield of the expected trimethylsilyl derivative as a somewhat hydrolytically unstable colorless oil (b.p. 105°/0.02 mm, *m/e* = 307). The ^{1}H NMR spectrum (60 MHz, 28°) of this material featured Me_3Si singlet absorptions at δ(CCl_4, TMS) 0.22 and 0.07, which were present in a relative ratio of 89/11 and had a total intensity corresponding to 9H, by comparison with the aromatic proton absorption at 7.23 (apparent s, 15H). Assignment of these Me_3Si signals to major and minor isomers (II) (89%) and (III) (11%), respectively, was based on the following spectroscopic observations.


(I)


(II) (III)

The IR spectrum of (II)/(III) revealed a strong P=O stretching absorption at ν($CHCl_3$) 1194 cm^{-1}, which was of comparable intensity and similar frequency to that exhibited by (I) (1188 cm^{-1}). No absorption in the P=N region[6] (1185-1325 cm^{-1}) was detectable; however, a N-Si stretch[7] at 933 cm^{-1} was present. A sample of (II)/(III) examined by ^{1}H-decoupled ^{31}P NMR (100 MHz, 30°) showed singlet absorptions at δ(CH_2Cl_2, external 85% H_3PO_4) − 5.2 and + 1.6 in a relative ratio of 89/11. The downfield chemical shift of the major resonance closely corresponds to that of (I) (δ − 6.5) and is therefore associated with (II), while the relatively upfield position of the weaker signal due to (III) is consistent with a rough estimate of the expected ^{31}P chemical shift in this

P=N tautomer.* Finally, it was found that addition of $Eu(fod)_3$ to either a carbon tetrachloride or benzene solution of (II)/(III) caused approximately 3-fold greater downfield-shifting of the major ^1H NMR Me_3Si singlet, relative to the minor Me_3Si singlet. Such an observation is consistent with these signals being respectively due to (II) and (III), given that a P=O group (as in (II)) is known[8] to effectively compete with other lone-pair donor sites (as in (III)) for complexation with $Eu(fod)_3$.

Thermodynamic aspects of (II) $\rightleftarrows$ (III) were investigated in α-bromonaphthalene solvent by use of variable temperature ^1H NMR over a range of 28-129°. Careful measurement of relative Me_3Si signal intensities obtained at different temperatures provided equilibrium constants ($\underline{K}$) that yielded a linear plot of $\ln \underline{K}$ vs. $\underline{T}^{-1}$, with $\Delta\underline{G}_o = 1.7$ kcal/mol being the ground state free energy change for (II) → (III) at 25°. The relative population changes for (II)/(III) from 89/11 (28°) to 80/20 (129°) were reversible and reproducible. While this experimental $\Delta\underline{G}_o$ value is somewhat smaller than the enthalpy change of 7.2 kcal/mol estimated by Glidewell[4] for *N*-silyl → O-silyl tautomerization in a phosphoramidate, we have been unable to detect the *O*-trimethylsilyl tautomer of $(Me_2CHO)_2P(O)NPh(SiMe_3)$, which implies less of a discrepancy between actual and estimated thermodynamic data in this diisopropyl system. It is also apparent that the substituents bonded to phosphorus, and presumably nitrogen, can detectably influence the magnitude of $\Delta\underline{G}_o$ in silylated phosphoramidates.

Approximate lower and upper limiting values for free energies of activation for (II) $\rightleftarrows$ (III) were also obtained by ^1H NMR methods in α-bromonaphthalene solvent. Thus, our

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*Calculation of the ^{31}P chemical shift to be expected for (III) on the basis of published data is difficult, owing to the scarcity of closely comparable P=N systems; however, *N*-benzoyl- and *N*-*p*-toluenesulfonyl-*O*,*O*,*O*-triphenylphosphorimidate respectively exhibit[4] ^{31}P resonances at δ +2.0 and +21.7. In this connection, we note that δ values of −5.9 and −6.8 have been reported[4] for $(Me_2CHO)_2P(O)NCH_2Ph(SiMe_3)$ and $(Me_2CHO)_2P(O)NCH_2Ph(SiPh_3)$, respectively.

observation of sharp Me_3Si signals for (II) (80%) and (III) (20%) at 129° with $\Delta\nu = 12$ Hz indicates a minimum barrier height ($\Delta\underline{G}^\ddagger$) of $\sim$ 21 kcal/mol for (III) → (II).* On the other hand, an NMR sample of (II)/(III) thermally equilibrated at 22° required $\sim$ 5 min. to re-equilibrate after insertion into the spectrometer probe that was pre-heated at 129°. If an equilibration half-life of $\sim$ 1 min. is assumed, a value of $\Delta\underline{G}^\ddagger \sim 27$ kcal/mol obtains. Since bulk heat transfer per se requires $\sim$ 2-3 min., we believe that this latter estimate for $\Delta\underline{G}^\ddagger$ represents a generous upper limit. Sample dilution by a factor of two had no measurable effect on the re-equilibration time and therefore militates against conceivable bimolecular Me_3Si exchange processes.

The approximate bracketing values for $\Delta\underline{G}^\ddagger$ ($\sim$ 21-27 kcal/mol) of 1,3-trimethylsilyl migration in (II)/(III) are roughly comparable to those values measured in certain amide and thioamide analogs that exhibit relatively high barriers to 1,3-trimethylsilyl shift, as compared to more typical values of $\sim$ 10-20 kcal/mol.[1,2] Results of our investigations of substituent effects on $\Delta\underline{G}_0$ and $\Delta\underline{G}^\ddagger$, as well as the study of stereochemistry at silicon during migration will be reported in the future.

Acknowledgements

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*This minimum value simply derives from the assumption of signal coalescence for the unequally populated tautomers at 129° and application of appropriate dynamic NMR expressions (see footnote 23 in W. Egan, R. Tang, G. Zon, and K. Mislow, J. Amer. Chem. Soc., 93 (1971) 6205).

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