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REACTION OF PHENYL AZIDE WITH ORGANOSILICON HYDRIDES

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Singlet phenyl nitrene has proven to be extremely difficult to trap by intermolecular insertion into carbon-hydrogen bonds. Hall (1) has reported that the thermal decomposition of phenyl azide in cyclohexane at 180° yielded only 8°/₀ of N-phenylcyclohexylamine and that the reaction with optically active 2-phenylbutane was not stereospecific in that the N-2-phenyl-2-butylaniline obtained (yield not specified) was 60 °/₀ racemized. These results, as well as the presence of a significant primary kinetic isotope effect, have been interpreted as an indication that the products which formally correspond to insertion of singlet phenyl nitrene into C-H bonds arise from a two-step reaction of triplet phenyl nitrene, the first step being hydrogen atom abstraction and the second being collapse of a radical pair.

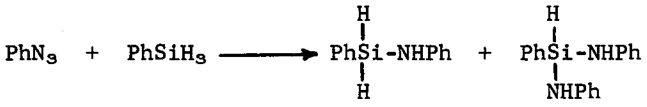
Since organosilicon hydrides have been shown to be quite reactive in respect to insertion into the Si-H bond by electron-deficient species, (2) we have examined the thermal decomposition of phenyl azide in the presence of organosilicon hydrides with the hope of trapping singlet phenyl nitrene prior to its relaxation to the triplet ground state.

Phenyl azide was dissolved in triethylsilane and the solution refluxed under nitrogen for 20 hr. On distillation N-phenyltriethylsilylamine was obtained in 38 °/₀ yield and its structure verified by comparison of its ir and nmr spectra with authentic material prepared as described by Anderson (3).

$$PhN_3 + Et_3SiH \longrightarrow PhNHSiEt_3 \quad (110°, 20\ hr)$$

There was no evidence for any reaction at the C-H bonds in Et_3SiH despite the 15:1 statistical factor in favor of C-H _vs_. Si-H insertion or abstraction. A small amount of aniline was detected by glpc and a control experiment demonstrated that no reaction occurred between aniline and triethylsilane under the reaction conditions.

A similar reaction was carried out in phenylsilane at reflux (119°) for 26 hr to afford, after distillation, two major products identified as N-phenylphenylsilylamine (**1**, 46°/o yield) and N,N'-diphenylphenylsilyldiamine (**2**, 18°/o yield). (4)



$$PhN_3 + PhSiH_3 \longrightarrow PhSiH_2\text{-}NHPh + PhSiH(NHPh)\text{-}NHPh$$

1 **2**

While it might appear from initial inspection of these results that efficient insertion of phenyl nitrene into Si-H bonds may have occurred there exists an important discrepancy which clearly rules out this possibility. From the reported (5) rates of thermal decomposition of phenyl azide the half-life at 105° is calculated to be _ca_. 500 hr and that at 115° to be _ca_. 140 hr. The yields of product obtained in the reactions described are too high to be compatible with a mechanism involving unimolecular decomposition of phenyl azide. A reasonable and likely alternative is an induced decomposition via the following chain sequence (6):

1) $PhN_3 \longrightarrow N_2 + Ph\text{-}\ddot{N}\!:$ (singlet)
2) $Ph\text{-}\ddot{N}\!:$ (singlet) $\longrightarrow Ph\text{-}\underset{\bullet}{\ddot{N}}\cdot$ (triplet)
3) $Ph\text{-}\underset{\bullet}{\ddot{N}}\cdot$ (triplet) $+ R_3SiH \longrightarrow Ph\text{-}\dot{N}H + R_3Si\cdot$
4) $R_3Si\cdot + PhN_3 \longrightarrow R_3Si\text{-}\dot{N}Ph + N_2$
5) $R_3Si\text{-}\dot{N}Ph + R_3SiH \longrightarrow R_3SiNHPh + R_3Si\cdot$

A similar mechanism can be suggested to explain the observation that phenyl azide and triphenyltin hydride react to form $PhNHSnPh_3$ in good yield in refluxing pentane except that in this case the initiation step is probably cleavage of the weak Sn-H bond. (7)

The stereospecificity of the reaction was investigated by adding phenyl azide slowly using a motor-driven syringe to (-)-α-naphthylphenylmethylsilane (3) ($[\alpha]_D$ -30.7°, 92% optically pure) (8) at 175° under nitrogen and heating for 20 hr. The desired product, N-phenyl-α-naphthylphenylmethylsilylamine (4) was isolated in 18% yield after chromatography on Activity I neutral alumina and found to have $[\alpha]_D$ -1.58° (pentane). Since optically pure 4 has a rotation of 27.6° and 3 and 4 of the same configuration have the same sign of rotation the reaction has occurred with a net 6% retention of configuration. (9) Repetition of the experiment gave 4 with 4% retention of configuration. A control experiment was carried out in which (+)-4 having $[\alpha]_D$ + 12.7° was heated with an equimolar amount of aniline at 160-175° for 20 hr. On recovery of 4 by column chromatography the rotation had decreased to + 8.55° which corresponds to 33% racemization under conditions approximating those of the reaction.

This observation of almost total racemization as the stereochemical course of reaction rules out concerted addition of phenyl nitrene and is in accord with the proposed chain process involving silyl radicals. By way of comparison, dichlorocarbene inserts into 3 with complete retention of configuration. (10) Recent reports (11) indicate that the silyl radical generated by hydrogen abstraction from 3 is chiral since it abstracts chlorine atoms from carbon tetrachloride to yield silyl chloride with predominant retention of configuration. In the reported reactions CCl_4 was present as solvent while in the reaction described here phenyl azide was added slowly to 3 which may have resulted in a condition where symmetrization of the radical at 175° was fast relative to reaction with the small amount of phenyl azide.

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