In conclusion, I represents an interesting case of a very simple, open-chain phenylhydrocarbon in which the relatively strong CD observed is without doubt only attributable to the optically active electronic transitions connected with the π system of a single phenyl chromophore. Considering the restricted conformational freedom of the molecule, the well-resolved CD and uv spectra should provide the basis for an improvement of theoretical treatments.

Acknowledgment. The authors wish to express their particular thanks to Dr. Alex F. Drake for helpful discussion and to Professor Enzo Benedetti for his skillful assistance in obtaining the ir spectra.

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(17) Nucleo di Ricerca del C.N.R., Pisa.

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N-Chloro-*N*-lithioaniline. Generation and Characterization of a Nitrenoid

Sir:

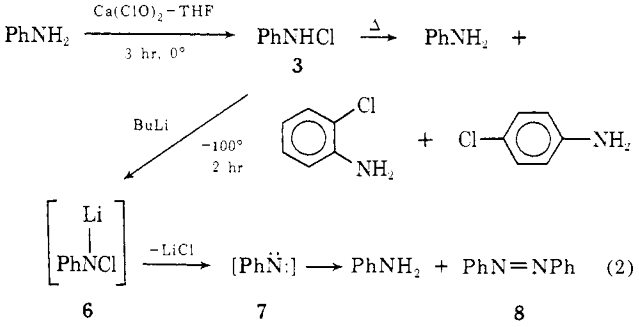
The similarities between nitrenes and carbenes are quite well known. Both intermediates can be generated by thermal or photochemical nitrogen elimination reactions: carbenes from diazo compounds and nitrenes from azides.[1] Another common method of producing carbenes is by the decomposition of α-chloroorganolithium compounds, carbenoids (RR′CLiX). Several of these carbenoids have been characterized at low temperatures.[2] The analogous nitrene generation *via* a "nitrenoid" intermediate (RNLiX) is not known.[3] The ready availability of amines has led us to investigate methods of efficiently producing nitrenes *via* α eliminations. This report deals with a proof of a nitrenoid intermediate and some nitrenium ion ($RN^{+}R'$) reactions.

Our first attempt at generating a nitrene by way of an α elimination is shown in eq 1. We were successful in obtaining *N*-bromoaniline (**1**), but lithiation of **1** gave only *n*-butylaniline (**2**) rather than proton abstraction.

$$\mathrm{PhNH_2} \xrightarrow[\text{2. Br}_2]{\text{1. BuLi-THF}} \underset{\mathbf{1}}{\mathrm{PhNHBr}} \xrightarrow[-100^\circ]{\text{BuLi}} \underset{\mathbf{2}}{\mathrm{PhNHBu}} \qquad (1)$$

Using a modification of Haberfeld and Paul's procedure,[4] aniline was chlorinated with calcium hypochlorite in tetrahydrofuran (THF) to give *N*-chloroaniline. After removal of the excess hypochlorite, the crude product (kept at 0°) was divided into two parts. The one part was allowed to decompose and gave (by vpc analysis) 64% aniline, 25% *o*-chloroaniline, 10% *p*-chloroaniline, and 1% of an unidentified component, probably dichloroaniline. This sets the lower limit of *N*-chloroaniline production at about 35%. There actually could be considerably more formed since the nitrenium ion intermediate that is presumably formed during the conversion of **3** to **4** and **5** may also hydrogen abstract from the solvent to give aniline.[5] The decomposition of *N*-chloroaniline in THF has not been previously examined. Attempts to get quantitative results by titration of the iodine liberated from the reaction of **3** and KI have not been successful (due to very poor end points).[4] It is, therefore, not possible to say how much aniline comes from nonreaction and how much from decomposition of **3** and, thus, what the exact yield of **3** was.

The other portion of the crude product was treated at −100° with 1 equiv of *n*-butyllithium for 2 hr and allowed to warm to room temperature. The solution warms smoothly with no sudden exotherm as is frequently observed in carbene generation.[2] The product consisted of 81.5% aniline and 18.5% azobenzene (**8**) and a small amount of polymer (eq 2). The production of aniline and azobenzene confirms that phenylnitrene was produced in these reactions, since phenylnitrene produced by the thermal or photochemical decomposition of phenyl azide also gives the same two products.[6]



Most nitrenes will add to olefins to give aziridines; however, phenylnitrene generated by photolysis does not.[7] [Phenyl azide will thermally add to olefins without prior loss of nitrogen.[8]] If the reactions outlined in eq 2 were conducted in the presence of a large excess of cyclohexene, aniline, azobenzene, and polymer were still the only products formed. Thus, phenylnitrene generated by α elimination shows the same reactions as phenylnitrene generated from phenyl azide.

The question now arises as to whether phenylnitrenoid (**6**) is an intermediate in these reactions or whether **3** goes directly to **7** by means of a concerted elimination of HCl. We have attempted to trap **6** in several ways.[9] The method that we found most successful was trapping with trimethylchlorosilane. A control experiment showed that trimethylchlorosilane does not react with aniline, *N*-chloroaniline, or *o*- and *p*-chloroaniline, but, if *n*-butyllithium was added to *N*-chloroaniline prior to or in the presence of trimethyl-

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(2) D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *J. Amer. Chem. Soc.*, **87**, 4147 (1965).

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(6) J. H. Hall, J. W. Hill, and H. Tsai, *Tetrahedron Lett.*, 2211 (1965).

(7) W. von E. Doering and R. A. Odum, *Tetrahedron*, **22**, 81 (1966).

(8) K. R. Henery-Logan and R. A. Clark, *Tetrahedron Lett.*, 801 (1968).

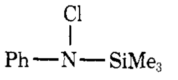
(9) Trapping with trimethyltin chloride, tributyltin chloride, methyl acetate, and triphenylphosphine has been unsuccessful; the same products appear as when no trapping agent was added.

chlorosilane, reaction did take place. The products of that reaction are shown in eq 3. It is significant to note that no azobenzene or trimethylbutylsilane (**11**) was found in either the reaction in which Me_3SiCl was added to the $PhNHCl$–$PhNH_2$ mixture or the one in which the Me_3SiCl was present *in situ* during the addition of the BuLi to the $PhNHCl$–$PhNH_2$ mixture.

$$PhNHCl + PhNH_2 \xrightarrow[\substack{Me_3SiCl\\ THF,\ -100^\circ}]{BuLi} PhNH_2 + \underset{\mathbf{9}}{PhNHSiMe_3} + \underset{\mathbf{10}}{PhN(SiMe_3)_2} \text{ and no } \mathbf{8}, \text{ BuSiMe}_3, \text{ or } \underset{\mathbf{11}}{\text{BuCl}} \quad (3)$$

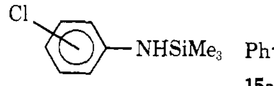
We have shown previously that the reaction of BuLi with Me_3SiCl at -100° occurs in the absence of acidic protons but is slow *relative* to proton abstraction from such things as methylene chloride or chloromethylsilanes.[10] Thus, the absence of **11** in the products of this reaction (eq 3) means that the BuLi preferentially reacted rapidly with $PhNHCl$ (and $PhNH_2$) rather than combining with Me_3SiCl. When BuLi reacts with $PhNHCl$, it must remove a proton rather than abstracting a chlorine since no butyl chloride or *N*-butylaniline (**2**), which could come from BuCl and PhNHLi, is found in the products. Since no azobenzene was produced in 2 hr contact of BuLi with $PhNHCl$ (and $PhNH_2$) at -100°, it follows that phenylnitrenoid (**6**) must have existed under those conditions.

The product of the silation trapping experiment was expected to be, initially, *N*-chloro-*N*-(trimethylsilyl)aniline (**12**). Upon warming, compound **12** was expected to rearrange, *via* the nitrenium ion **15**, to the ring-chlorinated products **13** and **14**. These latter two compounds were prepared by silation of *o*- and *p*-chloroaniline (*via* their lithium derivatives) and shown not to be present in the products of eq 3. It is possible, however, that the nitrenium ion intermediate was formed but that it reacted by way of hydrogen abstraction to afford the observed product **9**.



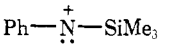
$$Ph-\overset{Cl}{\underset{}{N}}-SiMe_3$$

12



13, *o*-Cl

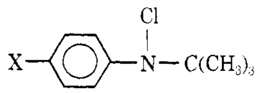
14, *p*-Cl



$$Ph-\overset{+}{\ddot{N}}-SiMe_3$$

15a, singlet state

b, triplet state

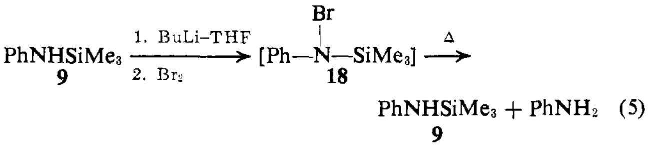


16

Gassman[5] has reported that decomposition of substituted *N*-chloroanilines (**16**) proceeds through nitrenium ions to give both ring-chlorinated and nonchlorinated anilines; in some cases the latter predominate. It is conceivable that the nitrenium ion **15** derived from **12** is very reactive, similar to some of Gassman's compounds, and decomposed by hydride abstraction from the solvent to afford **9** rather than rearranging to **13** and **14**.[11] Alternatively, the neighboring silicon may promote singlet to triplet interconversion of the nitrenium ion (**15a** → **15b**), which then undergoes hydrogen atom abstraction to give **9**. Gassman has shown that halogenated solvents promote singlet–triplet inversions in nitrenium ions and lead to large amounts of hydrogen atom abstraction.[12]

Several experiments have been attempted in order to determine how the nitrenium ion **15** might react in THF. One such attempt is shown in eq 4. The N–Si bond of *N*-trimethylsilylaniline-*N*-d_1 (**17**) is apparently easily cleaved by calcium hypochlorite, since the products of the reaction between these two reagents were aniline and hexamethyldisiloxane ($Me_3SiOSiMe_3$). Similar results were obtained with the protonated analog of **17**, both with THF and carbon tetrachloride as the solvent. In another attempt, *N*-bromo-*N*-trimethylsilylaniline (**18**) was generated as described in eq 5. The disappearance of the intense bromine color provided evidence that reaction had occurred; yet, as in the case of the chloro analog, no ring-halogenated products (or butyl bromide) were observed; only **9** and some aniline were found.

$$\underset{\mathbf{17}}{PhNDSiMe_3} + Ca(ClO)_2 \xrightarrow{?} \mathbf{12} \xrightarrow{?} \mathbf{15} \xrightarrow{?} \mathbf{9} \quad (4)$$



$$\underset{\mathbf{9}}{PhNHSiMe_3} \xrightarrow[2.\ Br_2]{1.\ BuLi-THF} \underset{\mathbf{18}}{[Ph-\overset{Br}{N}-SiMe_3]} \xrightarrow{\Delta} \underset{\mathbf{9}}{PhNHSiMe_3} + PhNH_2 \quad (5)$$

In summary, the silation results confirm that phenylnitrenoid **6** is a stable entity at -100° and can serve as a precursor of phenylnitrene. The principal product of the silation reaction, namely **9**, can be accounted for on the hypothesis of a nitrenium ion intermediate **15** reacting primarily by way of hydrogen abstraction from the solvent.

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(10) D. R. Dimmel, C. A. Wilkie, and F. Ramon, *J. Org. Chem.*, 37, 2662 (1972).

(11) Compound 10 probably arises by reaction of 9 with BuLi and, subsequently, Me_3SiCl.

(12) P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, **91**, 5176 (1969).

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Fluorination of Tetrasulfur Tetranitride and Hexamethylethane. An Indication of the Future of Direct Fluorination

Sir:

The recent development of a technique to control reactions of elemental fluorine with both inorganic and organic compounds has created a potential for synthesis of a large number of new compounds.[1] To illustrate the capabilities of this process in inorganic and organic synthesis, two very difficult problems, one inorganic and one organic, have been chosen for study.

Tetrasulfur tetranitride, S_4N_4, a delicate inorganic ring system, is shock sensitive to a degree that detonations of the pure compound have been observed.[2] Using more conventional techniques, the products of the reaction with fluorine are NSF, NSF_3, and $F_5SN=$

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(1) R. J. Lagow and J. L. Margrave, "The Reaction of Polynuclear Hydrocarbons with Elemental Fluorine," in press; R. J. Lagow and J. L. Margrave, *Chem. Eng. News*, **48**, 40 (Jan 12, 1970).

(2) M. Villena-Blanco and W. L. Jolly, *Inorg. Syn.*, **9**, 98 (1967).