Novel Synthesis of Phenyltrimethylsilyldiazene and Generation of the Phenyl Anion Synthon Therefrom

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Summary Oxidation of *N*-phenyl-*N'*-trimethylsilylhydrazine (**1**) with dimethyl azodicarboxylate gives high yields of phenyltrimethylsilyldiazene (**2**), which reacts with sodium methoxide in tetrahydrofuran to give the synthetic equivalent of the phenyl anion.

THE generation of carbon anions from diazenes is a process which is thought to occur in the Wolff–Kishner[1] reaction, and is well documented in the Bamford–Stevens reaction.[2] One can thus conclude that any compound which provides ready access to a diazene intermediate can potentially serve as a carbon anion synthon. In view of the immense heat of formation of nitrogen from diazenes, it is clear that diazene precursors can be expected to give rise to highly reactive anions under mild conditions. Phenyltrimethylsilyldiazene has proven to be just such a compound; the phenyl anion synthon has been generated by the comparatively weak base, sodium methoxide, and has been trapped with benzaldehyde, cyclohexanone, fluorenone, and benzophenone, giving the corresponding carbonyl addition products.

$$\underset{(\mathbf{1})}{\text{Ph–NH–NH–SiMe}_3} \xrightarrow{\text{i}} \underset{(\mathbf{2})}{\text{Ph–N=N–SiMe}_3} \xrightarrow{\text{ii}} \text{Ph–C(OH)R}^1\text{R}^2$$

SCHEME. i, $MeO_2C–N=N–CO_2Me$; ii, NaOMe, THF, R^1R^2CO.

Phenyltrimethylsilyldiazene[3] (**2**) is prepared in 90% yield by oxidation of the *N*-phenyl-*N'*-trimethylsilylhydrazine[4] (**1**) (Scheme) with dimethyl azodicarboxylate in light petroleum. In addition, preliminary work on alkyltrimethylsilyldiazenes indicates that this preparative method is general for a great variety of alkyl- and aryltrimethylsilyldiazenes.

The generation of the phenyl anion synthon is an easy process. To a mixture of 1 g of sodium methoxide, 150 mg of benzaldehyde, and 25 ml of tetrahydrofuran (THF) was added 300 mg of phenyltrimethylsilyldiazene. The blue colour of the diazene disappeared rapidly with evolution of gas and 180 mg (65%, based on benzaldehyde) of pure benzhydrol was isolated. Moderate yields of adducts were obtained with fluorenone (65%), benzophenone (30%), and cyclohexanone (13%). Yields have not been optimized, and the scope and utility of this reaction awaits further study. Nevertheless, this observation represents the mildest mode of carbanion synthon generation known. Unambiguous spectral data have been obtained for all compounds.

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