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PREPARATION OF SILICA-SUPPORTED DIARYL KETONES FOR USE AS PHOTOSENSITIZERS: A NOVEL SYNTHETIC APPLICATION OF SILICA-SUPPORTED PHENYLLITHIUM *

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Summary

Reaction of silica-supported phenyllithium, $G{\equiv}SiC_6H_4Li$ (G = silica support) with p-$(CH_3)_2NC_6H_4CO_2CH_3$ gives a silica-supported diaryl ketone of the type $G{\equiv}SiC_6H_4COC_6H_4N(CH_3)_2$ which is an active sensitizer for the photoisomerization of norbornadiene to quadricyclane. A major side-reaction in this synthesis is the combination of two phenyllithium functionalities with one p-$(CH_3)_2NC_6H_4CO_2CH_3$ to give a silica-supported triarylcarbinol of the general type $(G{\equiv}SiC_6H_4)_2[(CH_3)_2NC_6H_4]COH$ thereby indicating the ineffectiveness of the silica matrix at isolating the phenyllithium sites. The silica-supported phenyllithium required for this synthesis can either be obtained by lithium-hydrogen exchange using the sequence $G{\equiv}SiCl \rightarrow G{\equiv}SiC_6H_5 \rightarrow G{\equiv}SiC_6H_4Li$ with n-butyllithium/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine as the metallating reagent or by lithium-halogen exchange using the sequence $G{\equiv}SiCl \rightarrow G{\equiv}SiC_6H_4Br$-$p \rightarrow G{\equiv}SiC_6H_4Li$ with n-butyllithium as the metallating reagent. The latter method involving lithium—halogen exchange appears to be preferable for this synthesis.

Introduction

A promising system for the chemical storage of solar energy involves coupling the photosensitized conversion of norbornadiene (I) to quadricyclane (II) with the catalyzed exothermic reversion of quadricyclane to norbornadiene as the energy-storage and energy-release steps [1—4], respectively. This system requires immobilization of the catalyst onto an insoluble support. Previous papers from this laboratory [5,6] have discussed the properties of such immobilized catalysts. In addition, immobilization of the sensitizer onto an insoluble

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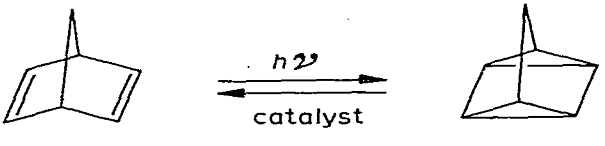

(I) (II)

support is also desirable for this energy storage system. Previous papers [1,7] have discussed the preparation and properties of polystyrene-supported diaryl ketone photosensitizers for the conversion of norbornadiene to quadricyclane. Such polystyrene-supported photosensitizers suffer from the drawback of facile photodegradation, presumably through hydrogen abstraction from the polymer backbone [8]. In order to avoid this difficulty we have begun to study a silica-supported diaryl ketone for use as photosensitizers for the conversion of quadricyclane to norbornadiene. This paper describes the methods used for the preparation of this silica-supported diaryl ketone. These methods are of potentially general interest to organometallic chemists since they involve the use of a novel silica-supported aryllithium reagent.

Experimental section

All reactions were performed under nitrogen in dried glassware that was thoroughly flushed with nitrogen before introduction of reactants. Syringes were used for chemical transfers and magnetic stirrers were used for agitation. Tetrahydrofuran and diethyl ether were distilled under nitrogen using potassium metal and $LiAlH_4$, respectively, as drying agents. For the attachment reactions to silica, a 500 ml round bottom flask was fitted with a frit to facilitate removal of reagents and washing of the silica.

Absorption spectra

Absorption spectra were taken with a Cary Model 15 UV-visible spectrophotometer. Heterogeneous samples of functionalized silica were diluted approximately 1 : 10 with unfunctionalized silica (in order to maintain an absorbance of less than 2). The silica mixture was placed in a 0.1 cm pathlength cuvette, and benzene was added to form a slurry. In certain cases small amounts of concentrated HCl were added as described. A reference cell containing unfunctionalized silica was similarly prepared.

Chlorinated silica gel, G≡Si—Cl

Silica gel (60—200 mesh), contained between two glass wool plugs in a 25 mm diameter pyrex tube placed in a Lindbert Hevi-Duty pyrolysis oven, was dried under a stream of nitrogen (50—300 ml/min) at 400 to 500°C for six hours. One end of the tube of silica was then connected to a flask of redistilled spectral grade carbon tetrachloride fitted with a nitrogen line, The other end of the tube was connected to an empty trap followed by three traps each containing 20% potassium hydroxide to trap the phosgene generated. Peri's method [9] was then used to convert the silica surface hydroxyls to chlorine by treatment with the carbon tetrachloride vapor in nitrogen at 450—550°C for about 20 h. Passage of nitrogen through the silica was continued for an additional 3 h at 300°C in order to remove any residual carbon tetrachloride.

The chlorine loading of the resulting chlorinated silica gel was determined by potentiometric titration with standardized sodium hydroxide of the hydrochloric acid liberated upon hydrolysis of the silica gel using a Corning Digital 112 Research pH meter. The chlorine content ranged from 1.22 to 1.55 meq Cl/gram of silica.

Silica-supported 4-N,N-dimethylaminobenzophenone, $G{\equiv}SiC_6H_4COC_6H_4N(CH_3)_2$

Two methods were investigated for the preparation of the silica-supported diaryl ketone which differed in the method of generating the silica-supported phenyllithium intermediate, $G{\equiv}SiC_6H_4Li$.

Method A (lithium—hydrogen exchange). A slurry of 4.99 g of chlorinated silica gel (total 7.58 meq chlorine) in 40 ml of dry degassed ether was stirred with 4.6 ml of phenyllithium (1.8 *M* in benzene; 8.3 mmol). The reaction was stirred for 1 h at room temperature giving a clear solution and light brown silica gel. The mixture was filtered, the silica washed three times for five minutes, each with 30 ml portions of ether. Silica gel was then dried under vacuum and 40 ml of cyclohexane was introduced. n-Butyllithium (1.0 ml of 1.6 *M* solution in hexane) was introduced followed by 0.5 ml (5.6 mmol) TMEDA. After 30 min of stirring, the orange silica was filtered and washed two times with 30 ml portions of ether. Then a 40 ml portion of THF was introduced. A solution containing 5.1 g (29 mmol) of methyl 4-(*N*,*N*-dimethylamino)benzoate in 30 ml THF was prepared in a separate flask under nitrogen. This solution was added to the silica gel which first turned green and then yellow. After two hours stirring the reaction was quenched with 5 ml of glacial acidic acid. Following 30 min of stirring the mixture was filtered in air, the silica washed 3 times with THF, twice with pentane and then air-dried.

The ultraviolet spectrum of the silica-supported *N*,*N*-dimethylaminobenzophenone prepared by this method exhibited a broad ultraviolet absorption band maximizing around 315 nm, for the diaryl ketone functionality. Nevertheless it was a moderately effective sensitizer for the photoisomerization of norbornadiene to quadricyclane giving a quantum yield of 0.154 ± 0.005 for a 1 *M* solution of norbornadiene in benzene irradiated at 366 nm. Controls with various silica materials lacking this complete procedure were totally ineffective as photosensitizers.

Method B (lithium—halogen exchange). A slurry of 2.0 g of chlorinated silica gel (total 2.44 meq Cl) in 25 ml of diethyl ether was treated with a cold solution of *p*-bromophenyllithium prepared by the addition of 1.6 ml (2.56 mmol) of 1.6 *M* n-butyllithium to 3.6 g (15.36 mmol) of *p*-dibromobenzene in 30 ml of diethyl ether followed by 1 h of stirring. After stirring for 1 to 3 h, the liquids were removed from the silica by filtration followed by three washings with diethyl ether. A slurry of the resulting *p*-bromophenylsilica, $G{\equiv}SiC_6H_4Br$, in 25 ml of diethyl ether was treated with 1.6 ml (2.56 mmol) of 1.6 *M* n-butyllithium. The slurry turned light brown in an exothermic reaction. After stirring for 45 min, the liquid was removed by filtration. The resulting silica was washed twice with diethyl ether and then suspended in 20 ml of tetrahydrofuran. A solution of 1.77 g (9.9 mmol) of methyl *p*-*N*,*N*-dimethylaminobenzoate in 10 ml of tetrahydrofuran was added quickly. The mixture turned very dark. The reaction was quenched with 5 ml of glacial acetic acid and stirred for 1 h after which the mixture appeared red-orange to dark red. The silica was filtered, washed with tetrahydrofuran, and placed in 50 ml of 10/1 tetrahydrofuran/triethylamine. After stirring for 4 h, the resulting yellow mixture was filtered. The silica was washed with tetrahydrofuran and the above step was then repeated. Finally, the silica was filtered, washed with tetrahydrofuran and extracted overnight with 5% triethylamine in tetrahydrofuran in a Soxhlet apparatus. The final product was yellow.

The silica-supported *N,N*-dimethylaminobenzophenone prepared by this method had the following properties:

(1) Ultraviolet-visible spectrum: Maximum at 355 nm with a less intense maximum at ~480 nm as determined in a 1 : 10 dilution with unfunctionalized silica in benzene versus a similar suspension of unfunctionalized silica gel in 1 mm cells. Addition of 3 drops of concentrated hydrochloric acid to a tetrahydrofuran slurry gave a pink species exhibiting a maximum at 470 nm.

(2) Chemical analyses: C, 10.7; H, 1.8; N, 0.65 corresponding to a C/H/N ratio of 19.2/39.4/1.

(3) Photosensitization: The limiting quantum yield was 0.24 in benzene solution for the isomerization of norbornadiene to quadricyclane extrapolated to infinite norbornadiene concentration.

Silica-supported 4-N,N-dimethylaminotriphenyl carbinol

A suspension of 3.10 g of chlorinated silica gel (total 4.81 meq Cl) in diethyl ether was stirred for 1 h with 2.6 ml (4.91 mmol) of 1.8 *M* phenyllithium. The liquid was then removed by filtration and the resulting phenylsilica gel, $G{\equiv}SiC_6H_5$, was dried under vacuum.

A slurry of this phenylsilica in 20 ml of cyclohexane was lithiated by successive treatment with 2.0 ml (13.3 mmol) of *N,N,N',N'*-tetramethylethylenediamine and 3.0 ml of 1.6 *M* (4.8 mmoles) n-butyllithium. After stirring the mixture for 4 h the lithiated phenylsilica was filtered under nitrogen and washed twice with cyclohexane. The lithiated phenylsilica was then stirred for 2 h with a solution of 1.17 g (5.2 mmol) of 4-*N,N*-dimethylaminobenzophenone in 50 ml of diethyl ether and 50 ml of tetrahydrofuran. The reaction was then quenched by stirring for 20 min with acetic acid thereby turning a bright red. The resulting silica was washed twice with tetrahydrofuran and then stirred for 1 h with a mixture of 100 ml of tetrahydrofuran, 10 ml of triethylamine, and 1.0 ml of water. The silica was then purified by Soxhlet extraction for 1 h with tetrahydrofuran containing 5% triethylamine, drying in vacuum, Soxhlet extraction with acetone, and finally drying for 6 h in vacuum.

The absorption of this silica-supported triarylcarbinol in benzene exhibited a maximum at 475 nm.

Preparation of 4-trimethylsilyl-4'-N,N-dimethylaminobenzophenone [10]

A mixture of 73.4 g (0.50 mol) of *p*-dichlorobenzene, 67.5 ml (57.8 g, 0.53 mol) of $(CH_3)_3SiCl$, 12.83 g (0.52 mol) of magnesium turnings, a few crystals of iodine and 100 ml of diethyl ether was stirred overnight and then boiled under reflux for 6 h. Gas chromatographic analysis indicated only the presence of starting materials. Therefore 100 ml of tetrahydrofuran were added and the reaction mixture boiled under reflux for an additional 12 h. The unreacted magnesium metal was then destroyed by the addition of 2 *N* hydrochloric acid.

The organic layer was washed three times with 20% sodium hydroxide, dried over anhydrous sodium sulfate, and then distilled through a 10 × 0.5 cm Vigreux column, The fraction boiling at 100—160°C/20 mmHg was shown by gas chromatography to contain approximately 90% *p*-chlorophenyltrimethylsilane and 10% bis(trimethylsilyl)benzene.

This *p*-chlorophenyltrimethylsilane (19.3 g, 0.105 mol), 3.14 g (0.13 mol) of magnesium turnings, and 100 ml of tetrahydrofuran were boiled under reflux for 1 day. The resulting pale red solution was added to a solution of 27 g (0.18 mol) of 4-*N*,*N*-dimethylaminobenzaldehyde in 100 ml of tetrahydrofuran. An exothermic reaction occurred and the solution became yellow. After stirring for 6 h at room temperature and 2 h at the boiling point, the reaction mixture was acidified with 100 ml of 0.5 *N* hydrochloric acid. Excess acid was neutralized with sodium bicarbonate until evolution of CO_2 ceased. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed successively with 10% aqueous sodium hydroxide and saturated aqueous sodium chloride. After drying over sodium sulfate, the solvent was removed in vacuum to give a yellow oil. This oil was chromatographed twice on silica gel, using toluene and dichloromethane successively as the eluants. The fraction from the initial yellow band was recovered and recrystallized, in the dark, by allowing a solution of the material in 1/2 dichloromethane/heptane to partially evaporate over a period of several days, giving 7.5 g (27% yield) of yellow 4-trimethylsilyl-4′-*N*,*N*-dimethylaminobenzophenone; m.p. 89—90°C; infrared spectrum (CCl_4); ν(CO) 1650 cm^{-1}; ultraviolet spectrum (benzene): 341 nm (ϵ 22 000), proton NMR spectrum (CCl_4): δ 7.71 (doublet, 2 H), 7.61 (singlet, 4 H), 6.61 (doublet, 2 H), 3.01 (singlet, 6 H), 0.28 ppm (singlet, 9 H).

Anal. Found: C, 72.5; H, 7.9; N, 4.6. Calcd. for $C_{18}H_{23}NOSi$: C, 72.7; H, 7.8; N, 4.7%.

Results and discussion

The key step in the synthesis of the silica-supported diaryl ketone $G{\equiv}SiC_6H_4COC_6H_4N(CH_3)_2$ is the reaction of the silica-supported phenyllithium $G{\equiv}SiC_6H_4Li$ with the appropriate ester p-$(CH_3)_2NC_6H_4CO_2CH_3$. In this connection the following two questions are of interest: (1) The method of formation of the silica-supported phenyllithium; (2) Further reaction of the silica-supported diaryl ketone $G{\equiv}SiC_6H_4COC_6H_4N(CH_3)_2$ with an additional phenyllithium functionality to give a silica-supported triaryl carbinol $(G{\equiv}SiC_6H_4)_2[(CH_3)_2NC_6H_4]COH$.

The following two methods were investigated for the preparation of silica-supported phenyllithium $G{\equiv}SiC_6H_4Li$: (1) Lithium—hydrogen exchange on $G{\equiv}SiC_6H_5$ using n-butyllithium or phenyllithium in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; (2) Lithium—halogen exchange on $G{\equiv}SiC_6H_4Br$-*p* using n-butyllithium. The required $G{\equiv}SiC_6H_4Br$-*p* for the second method was obtained by action of *p*-bromophenyllithium on chlorinated silica gel. The second preparative method involving lithium—bromine exchange appeared to lead to a more highly functionalized sample of $G{\equiv}SiC_6H_4COC_6H_4N(CH_3)_2$ as indicated by a well-defined ultraviolet absorption band maximizing at 355 nm and a higher quantum yield in the photoisomerization of norbornadiene (I) to quadricyclane (II).

The further reaction of $G{\equiv}SiC_6H_4COC_6H_4N(CH_3)_2$ with silica-supported phenyllithium to give a carbinol $(G{\equiv}SiC_6H_4)_2[(CH_3)_2NC_6H_4]COH$ was a major difficulty in this synthesis indicating that the site isolation of the phenyllithium units on the silica matrix is insufficient to present two of the phenyllithium units from reacting with a single p-$(CH_3)_2NC_6H_4CO_2CH_3$ molecule. The formation of the carbinol was indicated by the red color (470 nm maximum in the electronic spectrum) obtained by treatment of a tetrahydrofuran slurry with concentrated hydrochloric acid. Similar spectral behavior was observed for a model silica-supported triarylcarbinol $G{\equiv}SiC_6H_4[(CH_3)_2NC_6H_5]COH$ synthesized by the reaction of $G{\equiv}SiC_6H_4Li$ with p-$(CH_3)_2NC_6H_4COC_6H_5$.

The $G{\equiv}SiC_6H_4COC_6H_4N(CH_3)_2$ prepared by lithium—halogen exchange (Method B in the Experimental Section) was characterized by its electronic absorption spectrum, emission spectrum [7], elemental analyses, and photosensitizer properties. The maximum in the electronic spectrum appeared at 355 nm as expected. The red shift of this maximum relative to the corresponding 341 nm maximum in the model compound p-$(CH_3)_3SiC_6H_4COC_6H_4N(CH_3)_2$-$p$ is a consequence of the relatively polar environment [7] of the silica matrix. Interestingly, when the silica-supported ketone is treated with trimethylsilyl chloride and pyridine to reduce the surface polarity, the absorption and emission maxima are blue shifted as expected [11]. Based on the typical extinction coefficient of this chromophore it is possible to calculate the extent of functionalization. Thus the silica-supported diaryl ketone contains 1.4×10^{-2} meq ketone/g silica. Since the nitrogen analysis corresponds to 4.6×10^{-1} meq N/g, silica, only a small portion of the nitrogen can arise from the diaryl ketone functionality. We thus regard the silica-supported diaryl ketone as a dilute solution of $G{\equiv}SiC_6H_4COC_6H_4N(CH_3)_2$ in the triarylcarbinol $(G{\equiv}SiC_6H_4)_2[(CH_3)_2NC_6H_4]$-COH. Despite the limited concentrations of active ketone functionalities in our silica-supported ketones as indicated by these experiments, these materials are active photosensitizers for the conversion of norbornadiene (I) to quadricyclane (II) as well as for other photochemical conversions. Further details on the photochemical and spectral properties of these systems are presented elsewhere [7].

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