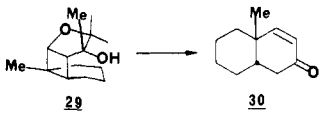
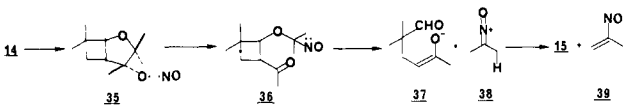
to the cyclohexenones **24** and **30** in yields of 74% and 92%, respectively, on nitrosation/irradiation followed by cyclodehydration.



29 **30**

Factors that facilitate Barton fragmentation[8] include stabilization of the derived carbon radical, particularly by oxygen,[14] as well as strain or steric compression in the initial alkoxy radical.[15] In the context of the present work, the mechanism outlined in eq 1 (**14** → **15**) is consistent with the available information.[16]



35 **36** **37** **38** **39**

The preceding discussion has presented an interesting and useful method for the elaboration of furanone/alkene photoadducts to cyclohexenones. The high material yields and regiochemical preferences of the photoaddition step when combined with the overall ease and efficiency of the fragmentation/cyclodehydration process recommends the reaction sequence as a general annelation technique.

Registry No. 3 ($R_1 = R_4 = H$, $R_2 = CH_3$, $R_3 = CH_2Bu$), 82555-03-1; **3** ($R_1 = R_2 = R_3 = R_4 = CH_3$), 82555-04-2; **3** ($R_1 = R_2 = (CH_2)_4$, $R_3 = R_4 = H$), 70147-91-0; **3** ($R_1 = R_2 = (CH_2)_3$, $R_3 = R_4 = H$), 70147-90-9; **3** ($R_1 = R_2 = (CH_2)_4$, $R_3 = CH_3$, $R_4 = H$), 82555-05-3; **3** ($R_1 = R_2 = (CH_2)_3$, $R_3 = CH_3$, $R_4 = H$), 82555-06-4; **3** ($R_1 = R_4 = H$, $R_2 = R_3 = (CH_2)_4$), 82526-75-8; **12**, 70147-92-1; **13**, 82555-07-5; **14**, 82555-08-6; **15**, 13544-11-1; **16**, 1073-13-8; **17**, 82555-09-7; **18**, 82555-10-0; **19**, 82555-11-1; **20**, 82555-12-2; **21**, 82555-13-3; **22**, 82555-14-4; **23**, 82555-15-5; **24**, 56140-62-6; **25**, 82555-16-6; *cis*-**36**, 55999-54-7; *trans*-**26**, 18317-63-0; **27**, 82555-17-7; **28**, 82555-18-8; **29**, 82555-19-9; **30**, 66964-45-2; **31**, 82555-20-2; **32**, 82555-21-3; **33**, 82555-22-4; **34**, 14523-53-6.

(13) Alcohol **29** is formed by the addition of methyllithium to a minor HT photoadduct between furanone **1** and methylcyclohexene, which was separated by chromatography.

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Sonochemical and Electrochemical Synthesis of Tetramesityldisilene

Philip Boudjouk,* Byung-Hee Han, and Kevin R. Anderson

Department of Chemistry, North Dakota State University Fargo, North Dakota 58105-5516

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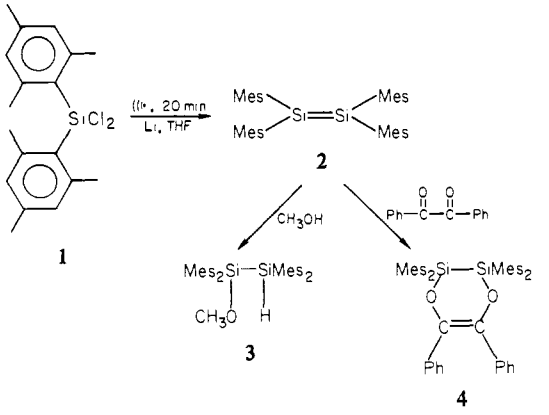
We have been investigating the effects of sonic waves on heterogeneous reactions, and we have observed some noteworthy rate enhancements.[1-4,7,10,16] For example, the Wurtz-type coupling of organic halides, RX (R = alkyl, aryl, benzyl, and benzoyl; X = Cl, Br, and I),[1] and organometallic chlorides, R_3MCl (R = alkyl, aryl; M = Si, Sn),[2] using lithium wire at room temperature proceeds at a convenient rate only in the presence of sonic waves. We have also found that sonication of a dioxane solution of α,α′-dibromo-*o*-xylene in the presence of zinc provides easy access to *o*-xylylene, a reactive intermediate that readily undergoes cycloaddition reactions to activated olefins,[3] and that ultrasound accelerates the Reformatsky reaction[4] requiring neither freshly prepared zinc powders[5] nor acid catalysts.[6] Significant rate enhancements of lithium aluminum hydride reductions of aryl halides,[7] the Barbier reaction,[8] the synthesis of thio amides,[9] and the catalytic reductions of olefins and ketones to hydrocarbons[10] point to considerable potential for sonic waves in synthesis.

In our earlier paper on the sonically accelerated couplings of silicon and tin halides[2] we reported the reaction of lithium with some simple dichlorosilanes to give high yields of cyclopolysilanes:

$$R_2SiCl_2 \xrightarrow[Li]{)))} (R_2Si)_n \qquad 70\text{-}95\%$$

R = Me, *n* = 6
R = Ph, *n* = 4

Prompted by the recent discovery by West et al.[11] that the silicon–silicon double bond can be stabilized by four mesityl groups, we extended our study to dimesityldichlorosilane (**1**). When a



1 **2** **3** **4**

solution of **1** in tetrahydrofuran (THF) was irradiated with ultrasonic waves in the presence of lithium wire, a yellow color was produced immediately, and within 20 min all of **1** and most of the lithium were consumed. Tetramesityldisilene (**2**) was isolated from the product mixture in ~90% crude yield. Purification by

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(12) In our hands, decomposition of **2** was extensive when sublimation or column chromatography was attempted, frustrating our efforts to remove traces of material containing Si-H and Si-OH linkages.

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crystallization from hexane gave yellow crystals with spectral features (NMR, IR, and mass) essentially identical with those reported by West.[11,12] When a solution of **2** was treated with methanol we obtained **3** in good yield. This compound was easily purified by column chromatography, and the assigned structure is supported by IR, NMR, and mass spectral data as well as elemental analyses. The addition of **2** to a THF solution of benzil gave a modest yield of the cycloaddition product **4**, a compound easily purified and characterized. IR, NMR, and mass spectral data and elemental analyses are consistent with the structure proposed for **4**. Analytically pure **3** and **4** were obtained in 72% and 38% yields, respectively, based on the quantity of **1**.

In a typical experiment, 1.5 mmol of **1** was added to a 100-mL round-bottomed single-necked flash containing 5 mL of dry THF (distilled from sodium benzophenone ketyl) and ≳3.0 mmol of lithium wire ($\sim^1/_4$ in. × 1/8 in. pieces) and partly submerged in a common ultrasound laboratory cleaner (117 V, 150 W, 50/60 Hz). After 20 min of sonication the yellow-orange product mixture was removed from the vessel by syringe and added to a warm solution of trapping agent.

For the methanol reaction the solution of **2** was added to excess dry methanol at 45 °C and maintained at this temperature for 30 min. The solvent and excess methanol were removed by flash evaporation, and methylene chloride was added. Filtration removed LiCl, and the product **3** was isolated by column chromatography (silica gel, 4:1 v/v pentane:CH_2Cl_2) to give 0.3 g (72%) of **3** as a pale yellow solid, mp 55–57 °C. The benzil quench was carried out in the same fashion by using a THF solution of excess benzil at 45 °C. The product, 1,2-diphenyl-4,4,5,5-tetramesityl-3,6-dioxo-4,5-disila-1-cyclohexene (**4**) was isolated as pale yellow crystals, mp 67–68 °C, following column chromatography.

The parallel between lithium-induced coupling reactions and electroreductive coupling reactions is obvious. In fact, a variety of chlorosilanes has been reduced to form disilanes by using constant-current electrolysis.[13] Dichlorosilanes give cyclopolysilanes under these conditions.[13] We have been investigating the electrosynthesis of polysilanes from chlorosilanes under controlled-potential conditions and have found that **1** produces **2** in a batch cell at −3.2 V vs. Ag/Ag^+.[14,15] We employed a 10-mL capacity, three-electrode divided cell with a mercury pool working electrode and a silver wire counter electrode. The electrolyte was tetrabutylammonium perchlorate dissolved in dimethoxyethane freshly distilled from sodium benzophenone ketyl. The half-wave potential of **1** was determined by differential pulse polarography at a dropping mercury electrode in the same solvent and found to be −2.8 V vs. Ag/Ag^+.

The amber product solution was treated with excess methanol, which discharged the color immediately. Removal of salts by crystallization was followed by column chromatography to give a 20% yield of analytically pure **2**. The reaction was carried out on 0.2 g of **1** at 40 mM.

We are investigating sonochemical and electrochemical routes to other novel organometallic species and will report our progress in due course.[16]

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Complete Analysis of Oligosaccharide Primary Structure Using Two-Dimensional High-Field Proton NMR

James H. Prestegard,† Theodore A. W. Koerner, Jr.,§ Peter C. Demou,† and Robert K. Yu*‡

Departments of Chemistry, Laboratory Medicine and Neurology
Yale University, New Haven, Connecticut 06510

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The emerging importance of cell-surface glycolipids and glycoproteins in membrane function has stimulated interest in new methods for the elucidation of the primary structure of the oligosaccharide moieties of glyco-conjugates. The potential utility of proton NMR spectroscopy in obtaining this type of data was long ago recognized,[1a] since this method is sensitive, rapid, quantitative, and nondestructive. To date, one-dimensional proton NMR methods[2] have yielded fragmentary data concerning the primary structure of underivatized oligosaccharides. Two-dimensional (2-D) homo- and heteronuclear NMR methods have been used as an aid in the assignment of the proton spectrum of a disaccharide.[1b] However, no generally applicable and systematic method for the complete analysis of oligosaccharide primary structure has resulted, largely because of the severe resolution problems that result when nearly all resonances of such substances fall within a two-ppm chemical shift range and because of the tedium associated with sequential spin decoupling and nuclear Overhauser effect (NOE) experiments needed to establish connectivities within spectra. Two recent advances overcome these limitations, namely the introduction of very high-field NMR spectrometers (500 MHz) and 2-D homonuclear correlated NMR methods,[3-5] first applied to the analysis of polypeptide spectra by Ernst, Wüthrich, and co-workers.[3,5] We now illustrate the systematic application of these new methods to the complete structural analysis of an oligosaccharide, using the glycolipid gangliotriaosylceramide (**1**, Figure 1) as an example.

Glycolipid **1** (1.0 mg), obtained by desialylation[6] of ganglioside G_{M2} from human brain, was dissolved in dimethyl-d_6 sulfoxide, deuterium oxide (0.5 mL, 98:2 v/v; 1.8 mM). Two types of 2-D NMR experiments were performed on a 500 MHz Bruker WM-500 NMR spectrometer. The first experiment,[3,4] 2-D spin-echo correlation spectroscopy (SECSY), which establishes scalar coupling (J) connectivities between peaks, was executed by using two 90° pulses separated by a time $^1/_2t_1$. The first time domain was formed by incrementing t_1. FIDs acquired at the end of time t_1 provide the second time domain. The data are displayed as a contour plot. Except for small displacements due to J coupling,

† Department of Chemistry.
§ Department of Laboratory Medicine.
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