the charge-transfer complex is favored, whereas electron-transfer occurs in high dielectric media. From previous work[3] it might be expected that complexation occurs through the chromium atom in tricarbonyltoluenechromium. The difficulties encountered in isolating complexes from media with high dielectric constants is a reflection of the fact that arenetricarbonylchromium compounds do not form stable cationic species; thus, the favored reaction in high dielectric media is the rapid formation of secondary products (eqn. 1). The isolation of a loosely bound complex of tricarbonyltoluenechromium with trinitrobenzene but not with the other Lewis acids studied, is consistent with the facts that trinitrobenzene is the weakest of these Lewis acids and that dibenzenechromium, which forms stable cationic species more readily than tricarbonyltoluenechromium, forms electron–transfer products with all the Lewis acids studied. The results reported here suggest that the charge-transfer complexes formed by tricarbonyltoluenechromium in media with low dielectric constants are loosely bound.

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1 C. FURLANI AND E. O. FISCHER, *Z. Elektrochem.*, 61 (1957) 481.
2 J. A. PAGE AND G. J. WILKINSON, *J. Am. Chem. Soc.*, 74 (1952) 6149.
3 J. W. FITCH, III, AND J. J. LAGOWSKI, *Inorg. Chem.*, 4 (1965) 864.
4 J. C. GOAN, E. BERG AND H. E. PODALL, *J. Org. Chem.*, 29 (1964) 975.
5 O. W. WEBSTER, W. MAHLER AND R. E. BENSON, *J. Am. Chem. Soc.*, 84 (1962) 3678.
6 B. NICHOLLS AND M. C. WHITING, *J. Chem. Soc.*, (1959) 551.
7 W. STROHMEIER, *Chem. Ber.*, 94 (1961) 2490.
8 R. FOSTER AND T. J. THOMPSON, *Trans. Faraday Soc.*, 58 (1962) 860.
9 R. E. MILLER AND W. F. K. WYNNE-JONES, *Nature*, 186 (1960) 148.
10 R. E. MILLER AND W. F. K. WYNNE-JONES, *J. Chem. Soc.*, (1959) 2375.

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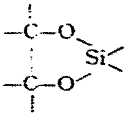
Cyclic esters of silicon containing a six-membered ring: (1,8-naphthalenedioxy)silanes*

Studies have been reported of five- and seven-membered heterocyclic systems containing silicon bonded through oxygen to aromatic rings[1,2]. It was found that the five-membered systems are in all cases less stable to hydrolysis and, while model studies show the  $\begin{matrix} -\overset{|}{C}-O\diagdown & \\ \vdots & Si\!< \\ -\underset{|}{C}-O\diagup & \end{matrix}$ ring to be sterically feasible, upon standing the five-

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[*] The *Ring Index* recommendation for these systems is either naphtho[1,8-*de*]-2-sila-*m*-dioxin or naphtho[1,8-*de*]-1,3,2-dioxasiline. In conformity with our previous reports, we name these compounds as derivatives of silane in this communication.

membered ring compounds exhibit a tendency toward ring-opening and polymerizati to materials from which monomer is regenerated upon distillation. This publicati describes the six-membered silicon cyclic esters fused to the 1,8-naphthalenedio system, as well as an improved method for obtaining the starting dihydric phen The preparation of the new five-membered cyclic ester, (*o*-phenylenedioxy)meth phenylsilane, is also reported.

Experimental

Analyses

Melting points were measured on a Townson & Mercer Type 5 melting poin block and are uncorrected. Molecular weights were determined on a Mechrolab Vapo Pressure Osmometer. Carbon, hydrogen, silicon and molecular weights were de termined by the Schwarzkopf-Microanalytical Laboratory. *o*-Phenylenedioxy methylphenylsilane was handled in a nitrogen-filled glove box of the usual type wit phosphorus pentoxide as the drying agent.

Preparation of 1,8-dihydroxynaphthalene

(*A*) 1-Naphthylamine-8-sulfonic acid (0.22 mole) was heated in 650 cc of 4% w/w potassium carbonate until the acid had been converted to its potassium salt. To the cooled salt solution (0°) was added 0.29 mole of sodium nitrite with constant stirring and this mixture was introduced into 50 cc of hydrochloric acid. The diazonium salt was heated for eight hours, during which time there was extensive bubbling due to the liberation of nitrogen. The crude naphthsultone produced was purified by treatment with benzene in a Soxhlet extractor. Potassium hydroxide (0.52 mole) was heated with 10 cc of water and 0.034 mole of the naphthsultone in a 250 ml nickel crucible to *ca.* 260° for 15–20 minutes. After cooling, the crude product was treated with 160 cc of 4 *N* hydrochloric acid and added to 500 ml of water. This aqueous solution was heated to dissolve the product and was filtered while hot. The filtrate, after cooling, afforded 1,8-dihydroxynaphthalene, m.p. 141–142°, in 80% yield.

(*B*) 1-Naphthol-8-sulfonic acid sodium salt (0.082 mole), 3 moles of sodium hydroxide pellets and 12 cc of water were heated at 240° for one hour in a 250 ml nickel crucible. After the melt had cooled, it was acidified with 300 cc of 18 *N* sulfuric acid. The mixture was diluted to 1.5 liters, then heated to dissolve the product and filtered. Upon cooling, long needle-like crystals (m.p. 141–142°) were obtained in poorer yields (*e.g.*, 18, 27 and 32% in three runs).

Esterification reactions

Bis(1,8-naphthalenedioxy)silane. To 1,8-dihydroxynaphthalene (0.032 mole) dissolved in 50 cc of dry ether, 0.016 mole of silicon tetrachloride was added in a nitrogen atmosphere. The evolution of hydrogen chloride served as an indication of reaction. Heating at ether reflux temperature was continued for 6.5 hours, during which time the solution became dark brown. Solvent was distilled and the product, m.p. 329–331°, obtained in 58% yield by sublimation *in vacuo* at 320°. (Found: C, 69.67; H, 3.66; Si, 7.98. $C_{20}H_{12}O_4Si$ calcd.: C, 69.76; H, 3.48; Si, 8.13%.) Insolubility precluded molecular weight determinations. Bis(1,8-naphthalenedioxy)silane is insoluble in alcohols and common organic solvents, but it is soluble in hot pyridine and dimethylformamide presumably due to complex formation*.

1,8-Naphthalenedioxydimethylsilane. To 1,8-dihydroxynaphthalene (0.0625 mole) partially dissolved in dry benzene, 0.0625 mole of dimethyldichlorosilane was added under a nitrogen atmosphere. The reaction was carried out with constant stirring until no further liberation of hydrogen chloride could be detected. The brown residue was sublimed *in vacuo* below 90° after distillation of solvent. White crystals, soluble in organic solvents, m.p. 53.5–55°, were obtained in ~ 7 % yield. (Found: C, 66.46; H, 5.51; Si, 12.92; mol. wt., 227. $C_{12}H_{12}O_2Si$ calcd.: C, 66.66; H, 5.55; Si, 12.96 %; mol. wt., 216.)

1,8-Naphthalenedioxydiphenylsilane. To 1,8-dihydroxynaphthalene (0.0625 mole) in 250 cc of dry ether was added 0.0625 mole diphenyldichlorosilane in a nitrogen atmosphere. The reaction continued with constant stirring for nine hours until there was no further indication of hydrogen chloride liberation. After removal of solvent the residue was sublimed *in vacuo* at 130° producing, in ~ 10 % yield, white crystals, m.p. 110–111°, which were soluble in common organic solvents. (Found: C, 77.70; H, 4.94; Si, 8.48; mol. wt., 330. $C_{22}H_{16}O_2Si$ calcd.: C, 77.64; H, 4.70; Si, 8.24 %; mol. wt., 340.)

o-Phenylenedioxymethylphenylsilane. Methylphenyldichlorosilane (0.25 mole) was added dropwise to a briskly stirred solution of 0.25 mole of catechol in refluxing dry ether under nitrogen and the mixture stirred until hydrogen chloride evolution was complete. Solvent was removed under reduced pressure, and the product distilled at 152°/1 mm to give a water-white, hygroscopic, viscous liquid. Only molecular weights corresponding to the dimer could be obtained from cryoscopic measurements in benzene. (Found: C, 68.85; H, 5.92 %; mol. wt., 424. $C_{13}H_{12}O_2Si$ calcd.: C, 68.4; H, 5.26 %; mol. wt., 228.)

Discussion

The preparation of 1,8-dihydroxynaphthalene has been previously reported in 43–57 % overall yield from 1-naphthylamine-8-sulfonic acid[3]. The modified procedure which we report results in the dihydric phenol in 80 % yield.

All the new six-membered ring systems can be handled in air without extensive hydrolysis. Like the organic starting material, 1,8-dihydroxynaphthalene, the six-membered silicon ring systems discolor over a period of time in air. The resulting dark brown solids retain their original infrared spectra, but have lower, longer range melting points, indicating some decomposition. For example, 1,8-naphthalenedioxydiphenylsilane, when freshly prepared, has a melting point 110–111°, but over a prolonged period the melting point is lowered to 101–107° due to contamination by oxidation products.

The six-membered ring systems resemble the seven-membered systems in that both are monomeric. The five-membered systems on the other hand, are subject to conversion to higher homologs. Schwarz and Kuchen reported the ester that resulted from the reaction between silicon tetrachloride and catechol to be tetrameric[4], and we have found that the dimethyl-[5], diphenyl-[5] and methylphenyl-silicon catecholate esters all undergo a reversible polymerization. These hydrolytically unstable esters

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* We have observed the formation of stable complexes between bis(o-phenylenedioxy)silane and these donor solvents (C. M. Silcox, and J. J. Zuckerman, unpublished results).

polymerize on standing to give, at first, more viscous liquids and then white solids.

We have previously found that molecular weight determination on samples of *o*-phenylenedioxydiphenylsilane purified in various ways gave evidence that the monomeric and dimeric species could be separated[2], and corroboration for this has come from another laboratory[6]. Only dimeric values were obtained for the liquid *o*-phenylenedioxymethylphenylsilane, however.

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1 J. J. ZUCKERMAN, *J. Chem. Soc.*, (1962) 873.
2 H. J. EMELÉUS AND J. J. ZUCKERMAN, *J. Organometal. Chem.*, 1 (1964) 328.
3 H. ERDMANN, *Ann. Chem.*, 247 (1888) 356.
4 R. SCHWARZ AND W. KUCHEN, *Z. Anorg. Chem.*, 266 (1951) 185.
5 H. J. EMELÉUS AND J. J. ZUCKERMAN, unpublished results.
6 A. J. NEALS AND B. B. MILLWARD, private communication, 1963.

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PRELIMINARY NOTES

The $n \rightarrow \pi^*$ transition of α-metal ketones

In a recent publication Harmish and West[1] proposed that the ultraviolet absorption spectra of α-silyl ketones could be explained on the basis of $d\pi$–$p\pi$ bonding involving the *d* orbitals of silicon and the π and π^* orbitals of the carbonyl group. West[2] has since generalized these proposals to predict the effect of metalloid substitution on the electronic transition of two- and three-atom chromophores.

Yates, Agolini and Csizmadia[3,4] by LCAO calculations, have been able to predict the magnitude of the shifts produced in ketones of the type R_3SiCOR, R_3GeCOR, and $R_3SiCOSiR_3$ without invoking *d* orbital participation.

In addition they have found that in ketones of the type $(C_6H_5)_3MCOC_6H_5$ that the base strength of the ketone decreased in the order Si > Ge > C, indicating that in the ground state the predominant effect is inductive release of electrons to the oxygen atom, rather than electron withdrawal through $d\pi$–$p\pi$ bonding[3,4].

Since it is generally agreed[5] that the amount of $d\pi$–$p\pi$ bonding should be successively less in germanium and tin compounds than in silicon compounds, it seemed of value to prepare a series of ketones $(C_6H_5)_3MCOCH_3$, M = C, Si, Ge and Sn, to gain