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DIRECT TRANSFER OF ALIPHATIC AND AROMATIC SUBSTITUENTS FROM ORGANOSILATRANES TO MERCURY(II) SPECIES

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Summary

The relative reaction rates of several silatranes (derivatives of 2,8,9-trioxa-5-aza-1-silatricyclo[3.3.3.$0^{1,5}$]undecane) and $HgCl_2$ in acetone-d_6 to yield the corresponding organomercury compound are of the order of e.g., 5×10^{-1} l mol^{-1} sec^{-1} or slightly less, a rate that is unexpectedly high compared to the essentially inert parent organotrialkoxysilanes. Thus, the apical Si–C bond of the silatrane is extraordinarily susceptible to direct electrophilic attack by mercury(II). The rates decrease in the order CH_2=CH, C_6H_5, *p*-ClC_6H_4 > CH_3 > CH_3CH_2, $CH_3CH_2CH_2$ > C_6H_{11}, $ClCH_2$, Cl_2CH, CH_3CH_2O. The effects of varying the solvent and the counterions are noted, and the probable mechanism is discussed.

Introduction

Organosilatranes, despite the presence of three deactivating oxygen substituents on silicon, are readily susceptible to electrophilic attack by mercury(II) to yield the corresponding organomercurial species. Silatranes (derivatives of 2,8,9-trioxa-5-aza-1-silatricyclo[3,3,3,$0^{1,5}$]undecane) are a class of pentacoordinate organosilicon compounds characterized by transannular donation of electron density from the 5-nitrogen to the silicon atom, thereby producing an effective penta-coordination at silicon [1–4]. The short Si–N distance reported [3] in silatranes, $RSi(OCH_2CH_2)_3N$, is consistent with a dative σ bond from N to Si and provides the silatranes their distinctive concavo-convex cage structure [2,3]. We would like to report that the apical Si–C bond is extraordinarily susceptible to direct electrophilic attack by mercury(II) to form the corresponding organomercurial compounds in protic or aprotic media:

$$RSi(OCH_2CH_2)_3N + HgX_2 \rightarrow RHgX + XSi(OCH_2CH_2)_3N$$

(R = alkyl, aryl; X = Cl, I, $C_2H_3O_2$).

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It is most important to note that the parent organotrialkoxysilanes are essentially inert under similar reaction conditions [5]. Also, there is no need for prior hydrolysis and conversion of the silatranes to organopentafluorosilicates, previously reported as a required intermediate step for reaction with mercury(II) [6]. As originally noted by Frye et al. [1] the resulting Si–Cl bond appears to be unusually stable in methanol, and this stability also occurs in aqueous media as well. This persistence of Si–Cl bonds provides a means of "sequestering" chloride ions with a resulting influence on the rate of the reaction [7].

Experimental

The silatranes, except for the phenylsilatrane kindly supplied by Dr. Martel Zeldin, were prepared from the appropriate trialkoxysilanes by methods similar to those described by Frye [8].

In a typical experiment utilizing the modified Frye method [8], 8.21 g (0.0500 mol) of triethoxysilane were added to 7.45 g (0.0500 mol) of triethanolamine in 50 ml of xylene and brought to a gentle reflux. After 2 h, the solution was filtered while hot and the silatrane allowed to crystallize. Recrystallization from $CHCl_3$ produced a 20% yield of silatrane.

Silatrane can be synthesized in better yields by using a modification of the method described by Voronkov [9]. In a typical experiment, 8.22 g (0.0500 mol) of triethoxysilane were added in 50 ml of xylene to 7.83 g (0.0500 mol) of boratrane (vide infra). A catalytic amount of Al_2Cl_6 (0.05 g) was also added to the solution in order to promote alkoxy ligand redistribution. The procedure utilized above then produced the thermodynamically more stable silatrane in 70% yield. M.p. 254–256°C.

Boratrane ($B[OCH_2CH_2]_3N$) was prepared by a modification of the method of Craddock et al. [10] 6.18 g (0.100 mol) of boric acid was added to 14.9 g (0.100 mol) of triethanolamine in 25 ml of xylene and heated to reflux. After 5 ml H_2O had been collected (theoretical 5.4 g), the solution was filtered while hot. The boratrane crystals (m.p. 227°C) were recrystallized from acetone and stored under N_2 until used.

The boratrane (Voronkov) method was also found to be best for the preparation of chlorosilatrane (50% yield; m.p. 305°C) and ethynylsilatrane. In the latter case, boratrane crystals coprecipitated; however, ethynylsilatrane could not be isolated by the Frye method, apparently because it is unstable with respect to nuclear displacement by the ethanol produced in the Frye reaction.

The Frye method was successfully used for the preparation of the following silatrane derivatives: ethoxy (55%, m.p. 102°C), methyl (59%, m.p. 151–152°C), ethyl (68%, m.p. 132–133°C), n-propyl (41%, m.p. 82°C, recrystallized from CCl_4), cyclohexyl (72%, m.p. 160–161°C), vinyl (42%, m.p. 165–166°C), *p*-chlorophenyl (18%, m.p. 228°C), chloromethyl (82%, m.p. 208°C), and dichloromethyl (63%, m.p. 264°C).

It should be noted that the syntheses of the (chloromethyl)- and (dichloromethyl)-silatranes are vigorous reactions and should be conducted in an ice bath. The identities of the compounds were confirmed by elemental analyses and melting point determinations. The 100 MHz ^1H NMR data were obtained on a Varian XL-100 NMR spectrometer equipped with a Nicolet Multi-Observe Nuclei Accessory. The CW and pulsed FT-NMR ^1H spectra were run in water-d_2 or

acetone-d_6 using 5 mm NMR tubes. An internal deuterium lock was used with tetramethylsilane as the internal chemical shift standard. Data collection and processing were performed on a model 620/L-100 Varian Data Machine. The inversion recovery method was used to determine the longitudinal relaxation times (T_1) from which appropriate recovery times ($> 5T_1$ between pulses) were chosen for kinetic determinations.

Results and discussion

The relative reactivities of organosilatranes with mercury(II) species are shown in Table 1.

In acetone-d_6, the relative reaction rates between equimolar concentrations of $HgCl_2$ and organosilatrane were found to decrease in the following order: CH_2=CH, C_6H_5, p-ClC_6H_4 (fastest) > CH_3 > CH_3CH_2, $CH_3CH_2CH_2$ > C_6H_{11}, $ClCH_2$, Cl_2CH, CH_3CH_2O (slowest).

These results are in accord with the relative rates observed for Co–C bond cleavage by mercury(II) in organobis(dimethylglyoximato)cobalt(III) [11] and are a result both of electronic and of steric effects.

Among the saturated substituents, which as a class are less reactive, the ethyl and n-propyl groups were cleaved some three orders of magnitude more slowly than the methyl group. Free rotation of the ethyl and the n-propyl groups about the Si–C bond, and their compression against the silatrane cage during the transition state, sterically hinders flank attack by $HgCl_2$. The steric hindrance posed by the cyclohexyl

TABLE 1

RELATIVE REACTIVITY OF ORGANOSILATRANES WITH MERCURY(II) IN ACETONE-d_6

Silatrane substituent	Electrophile	Relative reaction rate
CH_3	$HgCl_2$	1 [a]
CH_3	$HgCl_2$	6×10^{-2} [b,c]
CH_3	$HgCl_2$	5×10^{-1}
CH_3	HgI_2	1×10^{-3}
$ClCH_2$	$HgCl_2$	[d]
Cl_2CH	$HgCl_2$	[d]
C_2H_5	$HgCl_2$	2×10^{-4}
C_3H_7	$HgCl_2$	2×10^{-4}
C_6H_{11}	$HgCl_2$	[d]
C_2H_3	$HgCl_2$	1.5
C_6H_5	$HgCl_2$	1.5
C_6H_5	HgI_2	8×10^{-2}
p-ClC_6H_4	$HgCl_2$	1.5
CH_3CH_2O	$HgCl_2$	[d]
CH_3	$SnCl_4$	[d]
CH_3	$Pb(NO_3)_2$	[d]
CH_3	$CdCl_2$	[d]
CH_3	$ZnCl_2$	[d]
CH_3	$FeCl_3$	[d]

[a] In water-d_2 solvent. [b] Apparent biomolecular rate constant = 4.0×10^{-3} l mol^{-1} s^{-1} at 35.0°C. [c] In methanol-d_4 solvent. [d] Relative reaction rate $< 1.5\times10^{-5}$.

group is so large that no cleavage was observed even under the forcing conditions of a 10-fold molar excess of $HgCl_2$ at 50°C. In the case of chlorinated aliphatic derivatives, not only does chlorine exert a similar steric effect, but it also inductively reduces the electron density of the Si–C bond, thereby rendering it essentially unreactive toward $HgCl_2$.

The unsaturated substituents can initially form a π-complex with $HgCl_2$ [12] which effectively eliminates the steric hindrance otherwise posed by these groups. Once held in close proximity to the Si–C bond, the mercury(II) now has a much greater probability of successful attack in a manner similar to the aliphatic reaction. The similar reactivity of the *p*-chlorophenyl derivative, which is discordant with the ring deactivating behavior of chlorine, could well be due to a compensating increase in transannular donation of electron density to silicon by nitrogen.

Methylsilatrane, $HgCl_2$, and the reaction product methylmercuric chloride are sufficiently soluble in D_2O and in methanol-d_4 to permit the effects of these solvents upon the reaction rate to be observed easily by FT-NMR. The results of these kinetic determinations are also given in Table 1.

The donor numbers of H_2O, acetone, and methanol are nearly equivalent (~17–18) [13], and thus the reaction might be expected to proceed most readily in the solvent possessing the highest dielectric constant (since this solvent would generate the largest percentage of the more reactive cationic chloromercury species). Although reaction was indeed found to proceed most rapidly in aqueous solution ($E = 81.0$), the rate of the reaction in d_4-methanol ($E = 31.2$) is considerably slower than in acetone ($E = 20.7$). Clearly, other factors such as specific solvent effects (i.e., hydrogen-bonding of methanol with the silatrane cage oxygens) play an important role in determining the rate of reaction [14].

The nature of the mercury(II) electrophile and the counterions present in solution can have a pronounced effect on the metathetical reaction rate. For example, the reactivity of HgI_2 was found to be substantially less than for $HgCl_2$, and no reaction was observed for the electrophiles CH_3Hg^+ and $C_6H_5Hg^+$ [15,16]. Other metal electrophiles were screened for reactivity with silatranes and no stable metal–methyl bonds were detected by ^1H NMR for zinc(II), cadmium(II), palladium(II), iron(II) or tin(IV) (see Table 1), although solvolysis of the silatrane cage to form triethanolamine occurred more rapidly in protic media in the presence of these electrophiles.

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