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Evidence for Exclusive General Base Assistance of Hydrolysis of *tert*-Butyldimethyl-(*m*-nitrophenoxy)silane by Oxyanions

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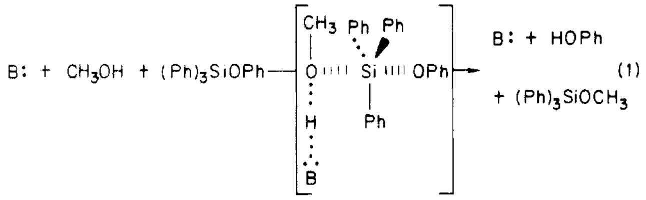
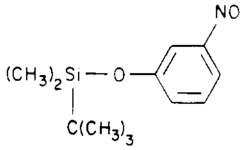
Some time ago Schowen and Latham reported that the methanolysis of (aryloxy)triphenylsilanes is subject to general base catalysis and that the reaction occurs by a concerted displacement (eq 1).[1] This finding was supported by subsequent work from the same laboratory which dealt with "hidden" solvent kinetic isotope effects in CH_3OH (CH_3OD)[2] and an apparent "push–pull" catalysis of methanolysis of $(CH_3O)(PhO)Si(CH_3)Ph$ by both components of a formate buffer.[3] Earlier work by Åkerman[4] showed that glycine buffer accelerated the solvolysis of R_3SiOPh ($R = CH_3$, C_2H_5, C_3H_7, n-C_4H_9, n-C_5H_{11}) in 51.4 wt % ethanol/H_2O.


(1)

On the other hand, Humffray and Ryan[5] in studying the hydrolysis of a series of meta- and para-substituted phenoxytriethylsilanes reported a Brønsted β_{LG}-value of 1.1 for buffer catalysis obtained by using two buffers (Tris and n-butylamine) in 60% aqueous dioxane. They concluded that it was probable that simultaneous nucleophilic and general base catalysis existed, in contradiction of Schowen and Latham's findings.[1a] Admittedly, the data on which the latter's conclusions were based included only three bases (acetate, phenoxide, and methoxide) which yielded a $\beta = 0.7 \pm 0.2$. Nevertheless, the observation that phenoxide catalyses the decomposition of phenoxytriphenylsilane requires a general base mechanism although the Brønsted correlation is probably not sufficiently precise to eliminate completely a nucleophilic pathway.

The hydrolysis of tris(2-methoxyethoxy)phenylsilane to phenylsilanetriol exhibits general base catalysis with a Brønsted β of 0.7.[6] In the latter study,[6] the observation that N-bases and O-bases fit the same Brønsted relationship was suggested to rule out an appreciable nucleophilic catalysis in that system. Finally, a recent report by Frye et al. indicates that the alcoholysis of Ph_2SiCl_2 and $Ph_2Si(OR)Cl$ in toluene is subject to nucleophilic catalysis (but not general base catalysis) by added tertiary amines.[7a] A double displacement mechanism was offered on the basis of these findings to explain Corriu's earlier observation that hydrolysis or alcoholysis of some optically active chlorosilanes gives products of retained configuration in the presence of HMPA, Me_2SO, or DMF.[7b]

In view of conflicting mechanistic details adumbrated above, we have undertaken a study of the solvolysis of *tert*-butyldimethyl-(*m*-nitrophenoxy)silane (**1**, BDNS) catalyzed by a series of oxyanions. This procedure is akin to that employed by Williams et al.[8] in their recent study of sulfonyl group transfer from 4-nitrophenyl 4-nitrobenzenesulfonate (**2**) to oxyanions in 10% dioxane/H_2O. While the latter reaction proceeds entirely by nucleophilic displacement, it will be seen that the hydrolysis of **1** in virtually the same medium proceeds entirely by a general base pathway.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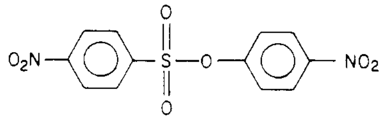
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Experimental Section

tert-Butyldimethyl(*m*-nitrophenyl)silane (**1**) was prepared in 65% isolated yield from the reaction of *tert*-butyldimethylchlorosilane with *m*-nitrophenol using imidazole as an HCl acceptor following the procedure of Cunico and Bodell:[9] bp 112 °C (1 torr); Ir (film) 2930, 1531, 1351, 1281, 1253, 960, 849 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 0.25 (s, 6 H), 1.0 (s, 9 H), 7.58 (m, 4 H); mass spectrum, m/z (relative intensity) 253 (19.5), 196 (100), 166 (9.2), 149 (29.2), 135 (8.6), 104 (4.7), 73 (7.15). Anal. Calcd for $C_{12}H_{19}NO_3Si$: C, 56.88; H, 7.56; N, 5.52. Found: C, 56.83; H, 7.56; N, 5.34.

Kinetics. The reaction of **1** in the presence of various oxyanions was measured spectrophotometrically with instrumentation previously described[10] by observing the rate of production of *m*-nitrophenoxide at 400 nm under pseudo-first-order conditions of excess oxyanion. The reaction was carried out in a solvent of 30% dioxane/H_2O (v/v) thermostated at 37.0 °C containing varying concentrations of half-neutralized oxyanion (as both buffer and base) at an ionic strength of 0.5 M (KCl). Second-order rate constants, k_{XO^-}, were evaluated from plots of the slopes of the pseudo-first-order rate constants vs. $[OX^-]$. At least five different concentrations of OX^- were used. It is important to note that the concentrations of oxyanions were held between 0 and 0.05 M; higher concentrations led to nonlinear Beer–Lambert plots. Self-association phenomena of phenols in mixed solvents is quite well-known[11] and therefore requires special attention to determine the maximum concentration of oxyanion that can be used. The intercepts of the plots yielded the uncatalyzed attack of solvent which appears to be linearly dependent on [OH], indicative of a process wherein hydroxide ion partakes in the reaction.

Special precautions were also required for the catechol and hydroquinone oxyanions, which rapidly oxidized unless the solutions were deaerated by bubbling argon through them for several hours prior to the introduction of the solid components.

Second-order rate constants for the hydrolysis of **1** catalyzed by imidazole and 4-(dimethylamino)pyridine were evaluated from slopes of plots of the pseudo-first-order rate constants vs. [free base].

Kinetics of Decomposition of 1 in the Presence of 1:1 *m*-Nitrophenol/*m*-Nitrophenoxide. Solutions of 200 mL of 30% dioxane/H_2O, ionic strength 0.5 M (KCl) containing 0.005–0.03 M *m*-nitrophenol were half-neutralized with KOH, thermostated at 37 °C, and innoculated with 0.5 mL of a stock solution of **1** in dioxane, to yield a final concentration 1×10^{-4}

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Table I. Second-Order Rate Constants for Base-Promoted Hydrolysis of 1 at 37 °C[a]

entry	X–OH	k_{XO^-},[b] $M^{-1}\ s^{-1}$	$pK_{a\,XOH}$[c]
1	CF_3CH_2	1.73 ± 0.05	13.5
2	2-HOC_6H_4	1.00 ± 0.04	13.8
3	Cl_3CCH_2	0.66 ± 0.03	13.2
4	2-C_5H_4N	0.44 ± 0.02	12.6
5	4-HOC_6H_4	0.42 ± 0.01	12.5
6	2,4-$(CH_3)_2C_6H_3$	0.19 ± 0.01	11.6
7	4-$CH_3C_6H_4$	0.130 ± 0.006	11.2
8	C_6H_5	$(6.6 \pm 0.2) \times 10^{-2}$	11.15
9	4-ClC_6H_4	$(3.6 \pm 0.1) \times 10^{-2}$	10.25
10	4-$CH_3CO_2C_6H_4$	$(1.08 \pm 0.1) \times 10^{-2}$	9.05
11	3-$NO_2C_6H_4$	$(1.08 \pm 0.11) \times 10^{-2}$	9.0[d]
12	2,4-$Cl_2C_6H_3$	$(8.45 \pm 0.43) \times 10^{-3}$	8.85
13	2,6-$Cl_2C_6H_3$	$(2.75 \pm 0.19) \times 10^{-3}$	7.8
14	C_6F_5	$(1.31 \pm 0.14) \times 10^{-3}$	6.6
15	succinate	$(1.13 \pm 0.13) \times 10^{-3}$	6.6
16	4-$N(CH_3)_2C_5H_4N$	$(1.02 \pm 0.08) \times 10^{-2}$	~9.5[e]
17	imidazole	$(9.2 \pm 0.7) \times 10^{-4}$	~7.0[e]

[a] Dioxane/H_2O (30%). [b] Error limits are standard deviations of plots of pseudo-first-order rate constants for appearance of *m*-nitrophenol vs. $[XO^-]$. k_2 for nitrogen base entries 16 and 17 refer to neutral base. [c] Entries 2, 5, 8, 9, 12, and 13 from ref 12. Other oxyanion entries pK_a's assumed to be 1.0 ± 0.4 units above pK_a in H_2O. [d] k_{XO^-} determined by kinetic decomposition of starting material. [e] pK_a values in H_2O. Values in 30% dioxane/H_2O expected to be lower by ~1.0 unit (see text).

M. At various time intervals, 20-mL aliquots were withdrawn and injected into a mixture of 20 mL of reagent grade cyclohexane and 10–20 mL of 0.1 N aqueous Na_2CO_3, the latter quantity being sufficient to neutralize the *m*-nitrophenol. Further washing of the cyclohexane layer with another 5–10-mL portion of Na_2CO_3 solution, 10 mL of dilute HCl, and 2 × 10 mL of H_2O was effected and the organic layer dried over $MgSO_4$. The absorbance of 3 mL of this solution in a 1.0-cm cell was recorded at 260 nm, and the data were plotted against time in the usual way to yield the pseudo-first-order rate constant for decomposition of 1. A plot of this rate constant vs. initial [*m*-nitrophenoxide] yielded a second-order rate constant, $k_{XO^-} = (1.08 \pm 0.11) \times 10^{-2}\ M^{-1}\ s^{-1}$ ($pK_a = 9.0$ in 30% dioxane/H_2O).

Results and Discussion

Given in Table I are the second-order rate constants (k_{XO^-}) for oxyanion-promoted decomposition of 1 in 30% dioxane/H_2O at 37 °C, as well as the pK_a values for the conjugate acids in the same solvent. The actual pK_a values for entries 2, 5, 8, 9, 12, and 13 have been determined[12] to be higher in 30% dioxane/H_2O than their values in H_2O, the average enhancement being 1.0 ± 0.4 units. The pK_a values for the remaining oxyanion entries in Table I have not been determined, but we assume the correction of 1.0 units to be reasonable for them as well since in all cases the charge type is the same. Also given in Table I are the observed second-order rate constants for the hydrolysis of 1 promoted by two nitrogen bases (entries 16 and 17). Their listed pK_a values are those determined in H_2O[13].

The oxyanion data are plotted to give the Brønsted relationship shown in Figure 1 and yield a linear relationship described by $\log k_{XO^-} = (0.43 \pm 0.01)pK_{XOH} - (5.9 \pm 0.1)$, $r = 0.995$. There is no apparent break in the line at $pK_{XOH} \simeq 9.0$, the pK_a of *m*-nitrophenol. This is consistent with the absence of a significant nucleophilic pathway under these conditions whereby oxyanion attack at silicon yields a five-coordinate reversibly formed intermediate even though such species are known for other silicon systems under different conditions.[14] Although not the case here, a linear plot could have arisen from a concerted nucleophilic displacement or a stepwise one wherein the intermediate exists in a shallow well at the top of the energy barrier.[8,15]

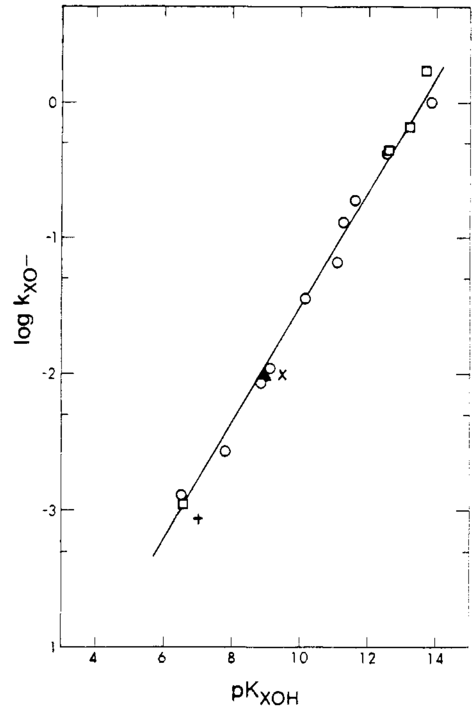

Figure 1. Plot of log k_{XO^-} vs. $pK_{a\,XOH}$ for the hydrolysis of *tert*-butyldimethyl-(*m*-nitrophenoxy)silane (1) catalyzed by various oxyanion buffers at 37 °C in 30% dioxane/H_2O, ionic strength 0.5 M. Phenoxides (○) in order of increasing pK_a are as follows: pentafluorophenolate; 2,6-dichlorophenolate; 2,4-dichlorophenolate; 4-chlorophenolate; phenolate; 4-methylphenolate; 2,4-dimethylphenolate; hydroquinone dianion; catechol dianion. non-phenolate oxyanions (□) in order of increasing pK_a are as follows: succinate, 4-pyridyloxy, trichloroethoxide; trifluoroethoxide; (▲) *m*-nitrophenoxy (see text); (+) imidazole; (×) 4-(dimethylamino)pyridine.

That the reaction actually involves exclusively a general base pathway is evidenced by three experimental results. First, *m*-nitrophenoxide ($pK_a \simeq 9.0$) catalyzes the decomposition of 1 with an observed $k_{XO^-} = 1.08 \times 10^{-2}\ M^{-1}\ s^{-1}$. This value fits the Brønsted correlation extremely well (identified as Δ in Figure 1) and suggests that the entire range of oxyanions act as general bases in 30% dioxane/H_2O. This conclusion corroborates Schowen and Lathams' similar conclusions although their solvent was methanol.[1] Also, the fact that the highly hindered 2,6-dichlorophenoxide anion fits on the Brønsted correlation indicates that the anticipated steric crowding which would result from direct substitution on silicon is absent in the transition state. Finally, we have observed that N-bases such as 4-(dimethylamino)pyridine and imidazole also catalyze the decomposition of 1. The observed second-order rate constants are $(1.02 \pm 0.08) \times 10^{-2}$ and $(9.2 \pm 0.7) \times 10^{-4}\ M^{-1}\ s^{-1}$, respectively. These data are located on Figure 1 as × and +, their pK_a values in H_2O of 9.5 and 7.0, respectively, being utilized. In actuality, these values should be reduced somewhat in the less polar medium used here, which should bring the points closer to the line. The demonstration that N- and O^--centered bases both fit the

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same Brønsted correlation argues strongly for a general base mechanism, since for a prominent nucleophilic pathway one would expect that anionic and neutral nucleophiles would have quite different reactivities.

There is no support for any significant nucleophilic role for the buffer components in the hydrolysis process. This is in contradiction of Humffray and Ryans' claims[5] but does corroborate the study of Pratt et al. although their substrate was a trisiloxane.[6] Quite likely, the source of the discrepancy in the former's work comes from the "rescaling" procedure used to compare data derived from two different buffer systems, *n*-butylamine and Tris.[5]

What is apparently curious is why the 4-nitrophenyl 4-nitrobenzenesulfonate studied by Williams et al.[8] in 10% aqueous dioxane undergoes direct nucleophilic substitution with many of the same oxyanions as used here. The preference between nucleophilic and general base routes for a given substrate undoubtedly depends upon a variety of complex effects such as steric accessibility, transition-state and ground-state solvation, and the electrophilicity of the substrate. We do not believe that the difference between the behavior of the silane and sulfoxide can be attributed to steric encumbrance in the former since Åkerman[4] reported general base catalysis of the hydrolysis of trimethylphenoxysilane, a much less sterically demanding system. More likely, in our opinion the transition state for oxyanion attack of the sulfonate ester is stabilized because the excess electron density is delocalized to the electronegative oxygens. On the other hand, since the silane has no such delocalization of charge possible, a general base pathway is favored, thereby avoiding the formation of large amounts of negative charge on Si in the transition state.

Acknowledgment. We are grateful to the University of Alberta and Natural Sciences and Engineering Research Council of Canada for financial assistance.

Registry No. 1, 98525-64-5; $CF_3CH_2O^-$, 24265-37-0; 2-$OC_6H_4O^{2-}$, 19021-48-8; $Cl_3CCH_2O^-$, 98525-65-6; 2-$C_5H_4NO^-$, 15473-97-9; 4-$OC_6H_4O^{2-}$, 48100-05-6; 2,4-$(CH_3)_2C_6H_3O^-$, 86260-38-0; 4-$CH_3C_6H_4O^-$, 22113-51-5; $C_6H_5O^-$, 3229-70-7; 4-$ClC_6H_4O^-$, 24573-38-4; 4-$CH_3CO_2C_6H_4O^-$, 98525-66-7; 3-$NO_2C_6H_4O^-$, 16554-54-4; 2,4-$Cl_2C_6H_3O^-$, 53678-12-9; 2,6-$Cl_2C_6H_3O^-$, 53330-27-1; $C_6F_5O^-$, 26910-95-2; 4-$N(CH_3)_2C_5H_4N$, 1122-58-3; succinate, 56-14-4; imidazole, 288-32-4.

Cyclopropanations of Alkenes Using Dibromomethane

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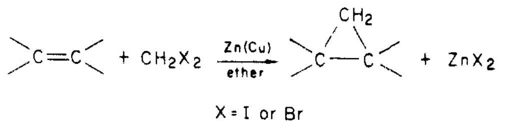
Although the utilization of diiodomethane in Simmons–Smith-type cyclopropanations of alkenes has been well established,[1] employment of the considerably less expensive, easier to purify and store dibromomethane has seldom been reported. This is primarily because the recommended procedure[1,2] for cyclopropanations employing dibromomethane specifies use of a separately prepared 30-mesh granular zinc–copper couple, involves long reaction times, and affords significantly lower isolated yields of cyclopropanation products than from corresponding diiodomethane reactions.



We now report a procedure using dibromomethane for cyclopropanation of alkenes which requires only short reaction times and also gives yields that are competitive with those obtained by using diiodomethane. This procedure utilizes sonocation of the reaction mixture in an ultrasonic cleaning bath to promote the heterogeneous zinc–copper couple reaction with dibromomethane through ultrasonically produced cavitation.[3-5] Also, it makes use of the convenient Rawson and Harrison zinc dust–cuprous chloride method[6] for generating the zinc–copper couple in situ.

Table I summarizes the results of cyclopropanations using dibromomethane and the present procedure on a number of representative alkenes. The data reveal the wide applicability of the procedure as well as its tolerance to various changes in experimental conditions. The yields of cyclopropanes isolated are generally competitive with those obtained with diiodomethane especially if one considers the fact that diiodomethane currently costs almost 20 times per mole greater than does dibromomethane and often requires repurification before use. Thus, for syntheses of cyclopropanes starting with readily available alkenes, the present procedure using dibromomethane is clearly the method of choice if expense is an important factor.

Experimental Section

General Procedures. Boiling points are uncorrected. ^1H NMR spectra were measured at 90 MHz with a Varian EM-390 spectrometer. Chemical shifts are reported in ppm downfield from Me_4Si and were referenced from Me_4Si and/or $CHCl_3$ internal standards. Zinc dust (Mallinckrodt), cuprous chloride (Mallinckrodt), dibromomethane (Aldrich), and anhydrous ether (Mallinckrodt) were used without further purification. The various alkenes were obtained commercially and redistilled before use.

General Procedure for Cyclopropanations Using CH_2Br_2. A 500-mL three-necked, round-bottomed flask is fitted with a Graham condenser and drying tube over an Allihn condenser and a pressure equalized dropping funnel and equipped for overhead mechanical stirring. Into the flask are added 52 g (0.80 mol) of zinc dust, 8.0 g (0.08 mol) of cuprous chloride, 75 mL of anhydrous ether, and 70 g (0.40 mol) of dibromomethane. To the addition funnel is added 0.20 mol of the alkene in 50 mL of anhydrous ether. The apparatus is positioned in a 125-W Branson ultrasonic bath which is filled to about 3 cm from the top with water preheated to 45–50 °C. Sonocation and stirring are started, and the position of the ultrasonic bath beneath the reaction vessel is varied so as to achieve maximum cavitation. Then the alkene is added dropwise to the reaction mixture over a 5–10-min period. After approximately a 1-h induction period, the reaction of the dibromomethane and zinc–copper couple usually starts. This is evidenced by a change in the color of the reaction mixture from gray to a purple-gray and by the onset of rapid refluxing. The stirring and sonocation are then continued for an additional 3 h.

As an alternative procedure, which results in a shorter induction period but otherwise has no major effect on the reaction, addition of the alkene is postponed until after the reaction of the zinc–

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