

Figure 4. The dependence of the deviations in the selectivities of basic nucleophiles, from the correlation in Figure 2, on the basicity of the nucleophile.

therefore, that it is time to terminate the debate as to whether or not the RSP exists. The problem is to identify, characterize, and interpret the changes that are observed in the hope that these will provide a better understanding of the nature of chemical reactions and their transition states.

**Values of  $\beta_{\text{nuc}}$  for Displacement by Amines.** The dependence on amine basicity of the rate constants for  $S_{\text{N}}2$  displacement on 4-nitrobenzyl tosylate is shown in the Bronsted-type plots of Figure 5. The slopes of the two lines do not differ significantly; the values of  $\beta_{\text{nuc}}$  are 0.31 for the substituted anilines and 0.26 for the aliphatic amines. This conclusion is different from that of an earlier study, in which values of  $\beta_{\text{nuc}} = 0.62$  for anilines and 0.20 for aliphatic amines were reported.<sup>48</sup> The reason for the difference in results is not clear, but the earlier results<sup>48</sup> were obtained from a comparison of rate constants in methanol with  $pK_{\text{a}}$  values in water, and the slope for anilines was heavily weighted by the rate constant for *p*-nitroaniline.

The very similar values of  $\beta_{\text{nuc}}$  for reactions of aliphatic amines and anilines provide no evidence for a different transition-state structure for these two classes of amines, which might arise from

(48) Koskikallio, J. *Acta Chem. Scand.* 1969, 23, 1490-1494.

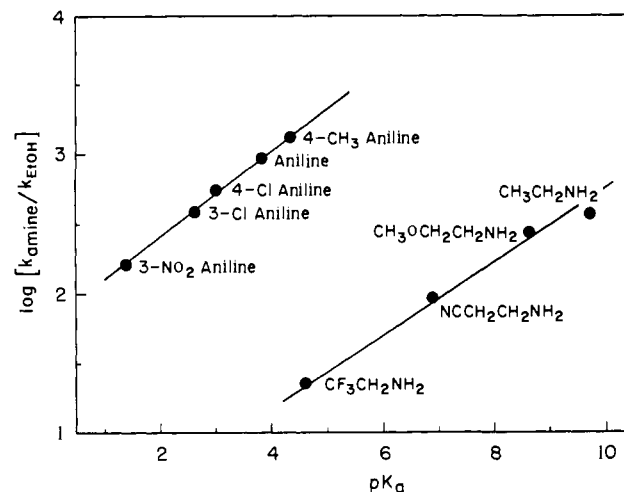


Figure 5. Bronsted-type plots for the reactivities of substituted anilines and aliphatic amines with 4-nitrobenzyl tosylate in 70:30 EtOH/HOH (v:v) at 25 °C.

resonance in the aniline series<sup>49</sup> for example. However, the absolute values of the rate constants are nearly two orders of magnitude larger for the anilines compared with the aliphatic amines, for a given basicity. The reactivity of phenoxide ion for nucleophilic substitution at carbon is also unusually large compared with that of the more basic methoxide ion,<sup>13</sup> and benzenethiolate anion is  $10^2$ - $10^4$  more reactive than methanethiolate anion in nucleophilic aromatic substitution with iodonitrobenzenes in methanol.<sup>50</sup> Stabilization of the transition state by interaction with the aromatic ring of phenoxide and arylthiolate anions could conceivably represent an interaction similar to the stabilization from the electron pair at the  $\alpha$  position of  $\alpha$ -effect nucleophiles in substitution at carbon.<sup>51</sup>

(49) Kovach, I. M.; Elrod, J. P.; Schowen, R. L. *J. Am. Chem. Soc.* 1980, 102, 7530-7534.

(50) Ho, K. C.; Miller, J.; Wang, K. W. *J. Chem. Soc. B* 1966, 310-314.

(51) Buncel, E.; Chuaqui, C.; Wilson, H. *J. Org. Chem.* 1980, 45, 3621-3626.

## Silylative Decarbonylation: A New Route to Arylsilanes<sup>1</sup>

Jonathan D. Rich

Contribution from General Electric Corporate Research and Development Center, Schenectady, New York 12301. Received January 6, 1989

**Abstract:** A new synthetic procedure for the preparation of aromatic chlorosilanes via the palladium-catalyzed reaction of methylchlorosilanes and aromatic acid chloride is described. The silylative decarbonylation process is solventless, can utilize low metal catalyst loadings (500-1000 ppm Pd), is carried out under moderate conditions (145 °C), and selectively gives aromatic chlorosilanes in good yield, generally 60-85%. The procedure is tolerant of a variety of aromatic substituents, for example, alkyl, halo, nitro, cyano, imide, acid anhydride, etc., and the synthesis of several new substituted aromatic chlorosilanes containing benzoyl chloride and phthalic anhydride moieties is described. Chloromethylsilane starting reagents are available from the direct reaction of methyl chloride and silicon, making this methodology an attractive synthetic route to functionalized aromatic chlorosilanes.

Aromatic chlorosilanes are employed in a wide variety of applications in the silicone industry.<sup>2</sup> While some arylsilanes can be prepared in the laboratory by utilizing aryl Grignard type reactions with chlorosilanes (within the usual constraints of

substituents which can tolerate such a method), only two synthetic procedures are currently practiced industrially: the direct reaction of chlorobenzene with silicon to yield primarily diphenyldichlorosilane (Rochow process)<sup>3</sup> and the boron trichloride catalyzed reaction between methylchlorosilane and benzene to give methylphenyldichlorosilane (Barry process).<sup>4,5</sup> There are undesirable

(1) (a) Rich, J. D. U.S. Pat. 4,709,054, 1987. (b) Rich, J. D. U.S. Pat. 4,604,477, 1986. (c) Preliminary results of this paper were given at the VIII International Symposium on Organosilicon Chemistry, June 7-12, 1987, St. Louis, MO.

(2) Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968; Chapters 8-10.

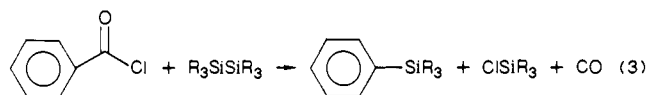
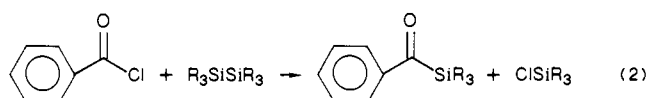
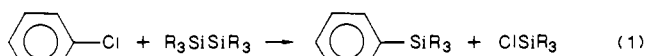
(3) (a) Rochow, E. G.; Gilliam, W. F. U.S. Pat. 2,380,995, 1945. (b) Rochow, E. G.; Gilliam, W. F. *J. Am. Chem. Soc.* 1945, 67, 1772.

(4) Barry, A. J.; Gilkey, J. W.; Hook, D. E. *Adv. Chem. Ser.* 1959, 23, 246.

aspects to each process, for example, formation of polychlorinated biphenyls in the former and the rather severe reactions conditions employed in the latter. Besides the above-mentioned problems, neither of the currently practiced processes is tolerant of other substituents on the aromatic ring and as such is suitable only for the preparation of unsubstituted phenylchlorosilanes.

An attractive alternative approach to arylsilanes by the metal-catalyzed reaction of chlorobenzene with disilanes was first described by Atwell and Bokerman in 1971 (see eq 1).<sup>6</sup> A simple calculation of the heat of reaction for eq 1 shows it to be exothermic by roughly 41 kcal/mol.<sup>7</sup> A recent series of studies by Nagai, Watanabe, and co-workers has demonstrated the generality of reaction 1.<sup>8</sup> Particularly interesting was the observation that nitro group substitution onto the aryl chloride led to greater reactivity and increased yield of arylsilane.<sup>9</sup>

In a related reaction, two groups reported that the palladium-catalyzed reaction between hexamethyldisilane and benzoyl chloride gave benzoyltrimethylsilane (eq 2).<sup>10,11</sup> In both examples, a small yield (3–7%) of phenyltrimethylsilane was found. The Japanese group also reported that *p*-nitrobenzoyl chloride gave an increased amount of decarbonylated product although the overall yield of the reaction decreased.<sup>12</sup>



In light of the above-mentioned results, a study was initiated to investigate the effect of substituents, particularly electron-withdrawing aromatic groups, on the reaction of disilanes with aromatic acid chlorides. In the course of this study it was found that the silylative decarbonylation reaction described in eq 3 could be made to completely predominate over the reaction in eq 2. In many aspects, this synthetic approach is superior to reaction 1 while in other cases the two processes yield complementary products (e.g., reaction with terephthaloyl chloride). This paper describes the overall synthetic scope of the silylative decarbonylation reaction.

## Results and Discussion

**(I) Effect of Aromatic Substituents on the Reaction of Benzoyl Chlorides with Hexamethyldisilane.** A series of reactions between aromatic acid chlorides containing substituents with increasing electron-withdrawing demand and hexamethyldisilane were investigated. In each reaction the acid chloride and disilane were heated neat to 125 °C for 24 h in the presence of 5 mol % bis(benzonitrile)palladium chloride and 10 mol % triphenylphosphine cocatalysts. The product ratios were determined by gas chromatography, and the results are summarized in Table I.

(5) Wright, A. *J. Organomet. Chem.* **1978**, *145*, 307, and references cited therein.

(6) (a) Atwell, W. H.; Bokerman, G. N. U.S. Pat. 3,772,447, 1971. (b) Atwell, W. H.; Bokerman, G. N. U.S. Pat. 3,746,732, 1971.

(7) Bond dissociation energies from Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(8) (a) Matsumoto, H.; Yoshihiro, K.; Nagashima, S.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1977**, *128*, 409. (b) Matsumoto, H.; Nagashima, S.; Yoshihiro, Y.; Nagai, Y. *J. Organomet. Chem.* **1975**, *85*, C1. (c) Matsumoto, H.; Nagai, Y. *Jpn. Kokai* 77/111540, 1976. (d) Nagai, Y.; Matsumoto, H. *Jpn. Kokai* 77/116442, 1976.

(9) Matsumoto, H.; Shono, K.; Nagai, Y. *J. Organomet. Chem.* **1981**, *208*, 145.

(10) Yamamoto, Y.; Suzuki, S.; Tsuji, J. *Tetrahedron Lett.* **1980**, 1653.

(11) Eaborn, C.; Griffiths, R.; Pidcock, A. *J. Organomet. Chem.* **1982**, *225*, 331.

(12) See Table I, footnote c, in ref 10.

**Table I.** Reaction of Hexamethyldisilane with Aromatic Acid Chlorides<sup>a</sup>



entry	R	% conv	% yield	
			RArCOSiMe <sub>3</sub>	RArSiMe <sub>3</sub>
a	H	72	79	5
b	<i>p</i> -OMe	64	86	0
c	<i>p</i> -Cl	61	75	0
d	<i>p</i> -NO <sub>2</sub>	100	28	18
e	3,4-dicarboxylic <i>N</i> - <i>n</i> -butylimide	97	49	42
f	3,4-dicarboxylic acid anhydride	97	23	64

<sup>a</sup>Reaction conditions: 125 °C/24 h; 5 mol % (PhCN)<sub>2</sub>PdCl<sub>2</sub>; 10 mol % PPh<sub>3</sub>.

When donor, neutral or weak electron-withdrawing para-substituted aromatic acid chlorides were investigated, palladium-catalyzed reaction with hexamethyldisilane gave predominately aromatic acylsilanes. Reaction of hexamethyldisilane with benzoyl chloride gave a 93/7 product ratio of benzoyltrimethylsilane to phenyltrimethylsilane. These results are nearly identical with those previously reported where tris(triphenylphosphine)palladium diiodide<sup>11</sup> or bis(π-allyl)palladium chloride/triethylphosphine catalyst systems were used.<sup>10,13</sup> *p*-Anisoyl chloride and *p*-chlorobenzoyl chloride yielded only acylsilane-containing products with hexamethyldisilane.

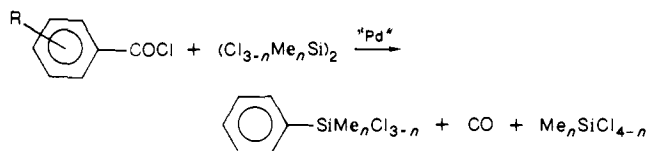
When strong electron-withdrawing aromatic acid chlorides were employed in the silylation process, the proportion of decarbonylated aromatic silane product increased correspondingly to the increasing withdrawing ability of the substituent. Reaction of *p*-nitrobenzoyl chloride with hexamethyldisilane gave a 29/18 ratio of (*p*-nitrobenzoyl)trimethylsilane to (*p*-nitrophenyl)trimethylsilane. Further increasing the electron-withdrawing ability of the substituent of *N*-*n*-butyltrimellitimidic acid chloride yielded a 49/42 ratio of acylsilane to arylsilane. Finally, in the case of trimellitic anhydride acid chloride, formation of the decarbonylated product, 4-(trimethylsilyl)phthalic anhydride, predominated over the corresponding acylsilane, 64/23.

The results of these experiments clearly established that the observed product ratio of arylsilane to acylsilane is directly proportional to the electron-withdrawing ability of the substituent placed on the aromatic acid chloride. A study was then initiated to determine if changing the nature of the groups attached to the disilane would also affect the course of the palladium-catalyzed reactions.

**(II) Effect of Silicon Substitution on the Reaction of Aromatic Acid Chlorides with Chlorinated Methylsilanes: 1,2-Dichlorotetramethyldisilane.** Reaction of equimolar amounts of benzoyl chloride with 1,2-dichlorotetramethyldisilane, using as standard reaction conditions no solvent, 145 °C, and the presence of 1 mol % bis(benzonitrile)palladium chloride and 2 mol % triphenylphosphine, quite remarkably and unexpectedly gave phenyldimethylchlorosilane as the *only* silicon-containing aromatic product in 89% isolated yield. One mole equivalent each of dimethyldichlorosilane and carbon monoxide also was formed during the reaction. None of the corresponding acylsilane, benzoyldimethylchlorosilane, could be detected as a product from the reaction mixture. This type of silylative decarbonylation process has been found to be quite general for a wide variety of aromatic acid chlorides reacting with chlorinated disilanes. The reaction is tolerant of various substituents which can be placed on the acid chloride, and in all cases examined to date, the process is completely specific for the formation of the decarbonylated arylchlorosilanes. A summary of palladium-catalyzed reactions of

(13) An extensive study of catalytic systems and the effect of donor ligand cocatalysts was carried out, and these findings will be reported in a subsequent article in this series. Within certain limitations, it was found that the exact catalyst nature had a more profound effect on the rate of reactions than it did on the observed product ratio of acylsilane to arylsilane.

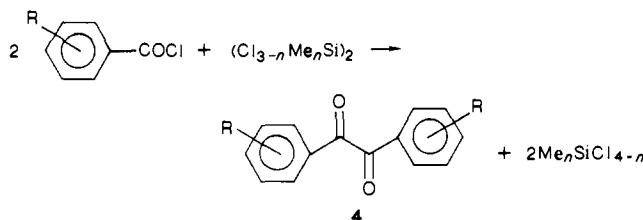
various aromatic acid chlorides with 1,2-dichlorotetramethyldisilane is shown in Table II:



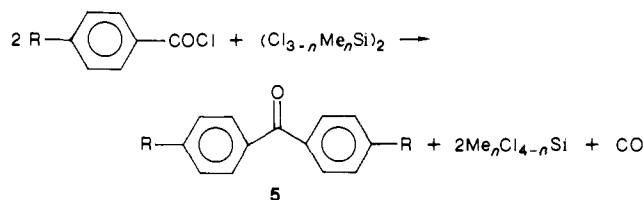
As a general rule, acid chlorides containing withdrawing substituents, e.g.,  $\text{NO}_2$ ,  $\text{CN}$ , etc., reacted at a fast rate and gave better yields of aromatic chlorosilanes than donor acyl chlorides. Also, yields of ortho-substituted aromatic silanes were considerably lower than those of the corresponding meta or para isomers. In all cases, the products were isolated by distillation from the reaction mixtures.

While the reactions were carried out under an atmosphere of nitrogen, no elaborate precautions were employed to exclude oxygen or moisture. The low-boiling chlorinated coproduct, dimethyldichlorosilane in the case of dichlorotetramethyldisilane, was removed continuously as it was formed. This prevented lowering of the reaction temperature caused by an increasing amount of low-boiling constituents and ensured a more rapid and complete reaction. The reactions could be carried out in high-boiling aprotic solvents such as *o*-xylene or anisole, but the solvent had no particular advantageous effect, and running the process neat was, in general, most convenient. A temperature of at least  $110^\circ\text{C}$  was required to initiate most reactions, and it was easiest to run the procedure at a temperature just below the boiling point of the disilane,  $145\text{--}155^\circ\text{C}$ , to facilitate removal of the chloromonosilane as it formed.

In most cases the yields of chlorodimethylarylsilanes were in the range of 60–80%. The major byproducts of the reactions, in 10–15% yield, were benzils:



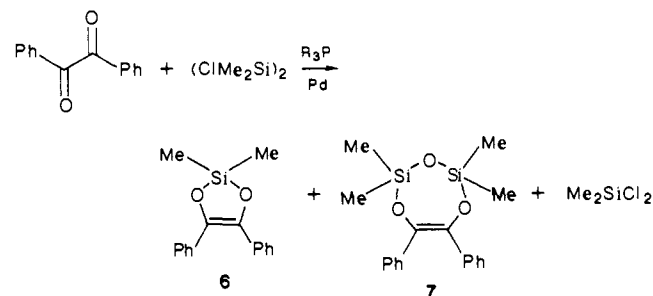
In the case of benzoyl chloride, benzil was isolated in 9% yield by distillation and recrystallization. The yield of 4,4'-dimethylbenzil was 18% from the reaction of *p*-toluoyl chloride and 1,2-dichlorotetramethyldisilane. A second byproduct, formed in much smaller amounts, was diaryl ketone:



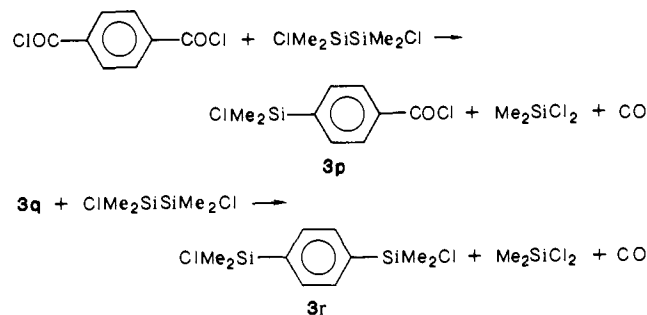
Benzophenone formed 2% of the product mixture in the reaction of benzoyl chloride. The proportion of side products seemed to increase with increasing electron-donating power of the substituent on the aromatic acid chloride. In the case of *p*-anisoyl chloride, some decarbonylation occurred without incorporation of silicon, and *p*-chloroanisole was found in 15% yield. Similarly, *m*-chlorotoluene was observed in 8% from the reaction of *m*-toluoyl chloride and 1,2-dichlorotetramethyldisilane.

The exact ratio of side products formed was found to be affected by the nature of the catalyst employed; for instance, some forms of supported heterogeneous catalysts could lead to predominance of benzophenone products, and the amount of benzil formed could be directly related to the donating ability of the added phosphine. The details of these experiments will be described in a future paper in this series. It is of synthetic interest to note that benzil further

reacted with 1,2-dichlorotetramethyldisilane in the presence of very strong donor phosphines such as tri-*n*-butylphosphine or tricyclohexylphosphine to give siloxanes **6** and **7**. This reaction only took place in the presence of the palladium catalyst:



The silylative decarbonylation process was first discovered in the reaction of dichlorotetramethyldisilane with terephthaloyl chloride. Reaction of 2 or more equiv of the disilane with terephthaloyl chloride gave 1,4-bis(dimethylchlorosilyl)benzene (**3r**) in 65% isolated yield. This compound is an important polymer precursor to the silphenylene family of silicone rubbers.<sup>14</sup> This reaction proceeded completely in two separate steps. Thermolysis of equimolar amounts of disilane and terephthaloyl chloride gave exclusively *p*-(chlorodimethylsilyl)benzoyl chloride (**3p**) (83% yield):



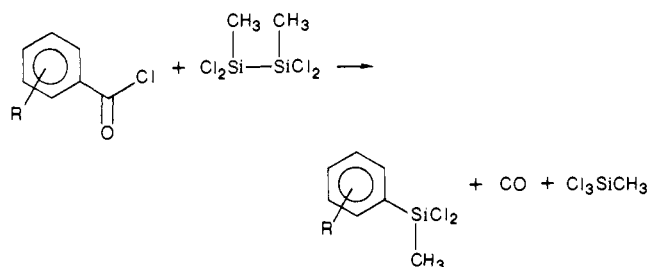
Similar results were obtained with isophthaloyl chloride. These observations were in accord with the results of a detailed study of aromatic acid chloride substituent effects on the rate of the silylative decarbonylation process. Those results will be disclosed in an accompanying paper in this series.

**(III) Reactions with *sym*-Tetrachlorodimethyldisilane.** Synthesis of methylchlorosilyl aromatic compounds from *sym*-tetrachlorodimethyldisilane is particularly important for two reasons. Dichloroarylsilanes allow incorporation of the aryl functional group into the backbone of a silicone polymer and as such are important for the preparation of graft copolymers, changing the solvent characteristics of silicones, or enhancing the thermal properties of silicone polymers. Second, *sym*-tetrachlorodimethyldisilane is readily available from Lewis acid catalyzed chlorodemethylation of disilanes formed in the direct reaction of methyl chloride and silicon.<sup>15</sup>

Reaction of *sym*-tetrachlorodimethyldisilane with trimellitic anhydride acid chloride utilizing standard reaction conditions, neat,  $145^\circ\text{C}$ , with 1% bis(benzonitrile)palladium chloride and 2% triphenylphosphine, gave 4-(dichloromethylsilyl)phthalic anhydride as a colorless liquid in 63% yield. Methyltrichlorosilane and carbon monoxide were also formed. Similarly, palladium-catalyzed reaction of *sym*-tetrachlorodimethyldisilane with *m*-nitrobenzoyl chloride gave *m*-(dichloromethylsilyl)nitrobenzene (70%), *p*-cyanobenzoyl chloride yielded (*p*-cyanophenyl)dichloromethylsilane (25%), and *N*-methyltrimellitimidic acid chloride gave *N*-methyl-4-(dichloromethylsilyl)trimellitimidic (15%):

(14) For a review of silphenylene rubber chemistry, see Rhein, R., Technical Reports NWC TP 6372, Oct 1983, NWC TP 6499, Oct 1984, and NWC TP 6593, Mar 1985; Naval Weapons Center: China Lake, CA 93555.

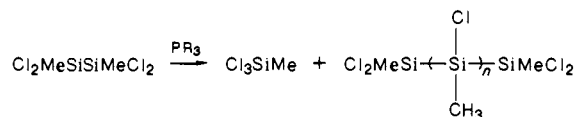
(15) Watanabe, H.; Kobayashi, M.; Koike, Y.; Nagashima, S.; Matsumoto, H.; Nagai, Y. *J. Organomet. Chem.* **1977**, *128*, 173.



R	yield (%)
1,2-O(C=O) <sub>2</sub>	63
1,2-CH <sub>3</sub> N(C=O) <sub>2</sub>	15
NO <sub>2</sub>	70
COCl	60
CN	25

As was observed with 1,2-dichlorotetramethyldisilane, reaction of equimolar amounts of *sym*-tetrachlorodimethyldisilane with terephthaloyl chloride gave exclusively the product from mono-silylation, *p*-(dichloromethylsilyl)benzoyl chloride (60% yield). Subsequent reaction with a second aliquot of disilane gave 1,4-bis(dichloromethylsilyl)benzene. Reaction of acid chlorides with tetrachlorodimethyldisilane was similar to that of 1,2-dichlorotetramethyldisilane in that acid chloride reactants containing electron-withdrawing substituents were more active and gave greater yields of silylated products than donor acid chlorides.

Unlike 1,2-dichlorotetramethyldisilane, reactions with *sym*-tetrachlorodisilane (or hexachlorodisilane) could be complicated by disproportionation of the polychlorodisilane without proper control of the reaction parameters. In general this meant running the reactions at the lowest temperature possible, 110–130 °C, and minimizing the phosphine cocatalyst concentration:



It was readily shown that this disproportionation reaction was caused exclusively by the presence of the added phosphine.<sup>16</sup> Thermolysis of *sym*-tetrachlorodimethyldisilane with bis(benzonitrile)palladium chloride under conditions similar to that utilized in the standard reaction, 145 °C, merely led to reduction of the palladium(II) catalyst to palladium(0) black. No disproportionation of the disilane occurred. Addition of triphenylphosphine under similar reaction parameters in the absence of the palladium material rapidly disproportionated the disilane.

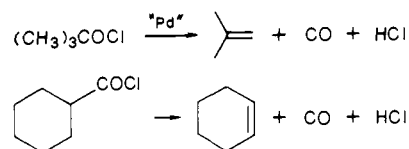
Catalysis of hexachlorodisilane with aromatic acid chlorides was similar to that of tetrachlorodimethyldisilane; for example, trimellitic anhydride acid chloride gave 4-(trichlorosilyl)phthalic anhydride; however, hexachlorodisilane also showed susceptibility to phosphine-catalyzed disproportionation if the reaction temperature was not carefully monitored.

**(IV) Exceptions to the General Reaction.** While, in general, aromatic acid chlorides react with chlorinated disilanes to give arylchlorosilanes via a silylative decarbonylation process, no examples of successful silylation of aliphatic acid chlorides were found. Careful examination of the palladium-catalyzed reaction of pivaloyl chloride with 1,2-dichlorotetramethyldisilane showed that 3 mol equiv of gaseous products formed instead of the expected one. The products were found to be isobutylene, HCl, and CO. The palladium-catalyzed  $\beta$ -hydrogen elimination reaction occurs with disregard for the presence of the disilane reagent.<sup>17</sup>

(16) Disproportionation of polychlorinated disilanes by phosphines or metallophosphines has been previously described. See (a) Calas, R.; Dunoques, J.; Delevis, G.; Duffaut, N. *J. Organomet. Chem.* **1982**, 225, 117. (b) Baney, R.; Gaul, J.; Hilty, T. *Organometallics* **1983**, 2, 859. (c) Matsumoto, H.; Okhawa, K.; Matsubara, I.; Kasahara, M.; Arai, T.; Nagai, Y. *J. Organomet. Chem.* **1984**, 264, 29.

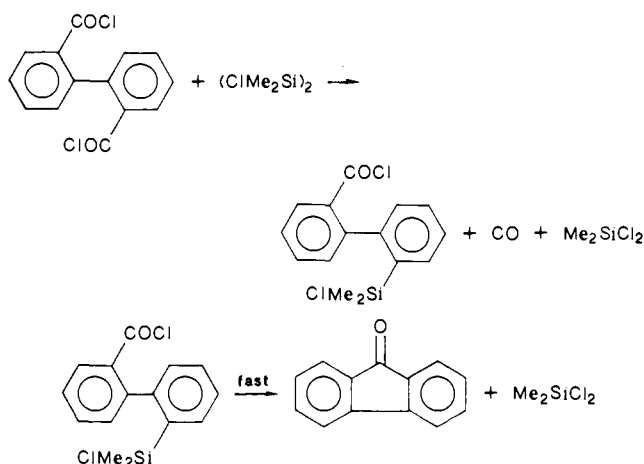
(17) See Tsuji, J. *Organic Synthesis via Metal Carbonyls*; Pino, P.; Wender, I., Eds.; Wiley-Interscience: New York, 1977; Vol. 2, pp 631–636, and references cited therein.

Similarly, cyclohexanecarboxylic acid chloride reacts in a known process to give cyclohexene:



A few examples of aromatic acid chlorides were found which did not give the usual silylative decarbonylation products. 2,6-Pyridinedicarboxylic acid chloride was recovered unreacted with 1,2-dichlorotetramethyldisilane under standard catalysis conditions. Introduction of bis(benzonitrile)palladium chloride to the mixture resulted in the formation of an uncharacteristic bright red solution, which suggests deactivation of the catalyst by formation of a hindered palladium–amine complex.

Addition of the catalyst mixture to a 1:2 molar ratio amount of diphenic acid dichloride and 1,2-dichlorotetramethyldisilane resulted in expulsion of carbon monoxide at a rate much greater than anticipated on the basis of other ortho-substituted acid chlorides. Workup of the reaction showed formation of 2 mol equiv of dimethyldichlorosilane but recovery of 1 mol equiv of unreacted disilane and isolation of fluorenone in 97% yield. The formation of this product can be explained by initial silylation of one of the aromatic rings to give 2-(chlorodimethylsilyl)-2'-biphenylcarboxylic acid chloride which can undergo a facile intramolecular Friedel–Crafts acylation to give the observed product:



## Conclusions

In conclusion, it has been found that the palladium-catalyzed reaction between aromatic acid chlorides and *disilanes containing at least one or more chlorine atoms* yields aromatic chlorosilanes. The silylative decarbonylation process is tolerant of a wide variety of substituents, giving aromatic chlorosilanes in good yield. The rate of reaction is clearly a function of the electron-withdrawing ability of the aromatic substituents. The product selectivity of acylsilane versus arylsilane is dominated by the presence or absence of chloro groups on the disilane reagent. Palladium catalyst loadings as low as 500 ppm have been employed successfully in large scale (>5 M) reactions, and the disilane reagents are readily available in large quantities from MCS direct process. The ease and scope of this reaction make this procedure the method of choice for the direct preparation of many aromatic chlorosilanes.

## Experimental Section

**General.** All acid chlorides utilized were commercially available except *N*-butyltrimellitimide acid chloride, which was readily prepared from trimellitic acid anhydride and *N*-butylamine followed by conversion to the acid chloride with thionyl chloride, and diphenic acid dichloride, which was prepared from commercially available diphenic acid. All materials were analyzed by gas chromatography prior to use and re-purified by distillation if the analysis showed less than 95% purity. The reactions are not tolerant of the presence of any free acids in the starting acid chloride materials.

**Table II.** Palladium-Catalyzed Reaction of Aromatic Acid Chlorides with 1,2-Dichlorotetramethyldisilane

entry	R	% conv	% RArSiMe <sub>2</sub> Cl
a	H	85	89
b	<i>o</i> -CH <sub>3</sub>	17	13
c	<i>m</i> -CH <sub>3</sub>	100	47
d	<i>p</i> -CH <sub>3</sub>	100	58
e	<i>o</i> -Cl	50	25
f	<i>m</i> -Cl	83	73
g	<i>p</i> -Cl	75	86
h	<i>o</i> -OMe	100	32
i	<i>m</i> -OMe	87	71
j	<i>p</i> -OMe	61	52
k	<i>m</i> -NO <sub>2</sub>	100	74
l	<i>p</i> -NO <sub>2</sub>	100	72
m	<i>p</i> -CN	87	77
n	<i>o</i> -COCl (1 equiv of disilane)	44	19 <sup>c</sup>
o	<i>m</i> -COCl (1 equiv of disilane)	87	61
p	<i>p</i> -COCl (1 equiv of disilane)	93	83
q	<i>m</i> -COCl (2 equiv of disilane)	<i>b</i>	66
r	<i>p</i> -COCl (2 equiv of disilane)	<i>b</i>	64
s	3,4-acid anhydride (trimellitic)	100	83

<sup>a</sup>0.5–1.0 mol % (PhCN)<sub>2</sub>PdCl<sub>2</sub>; 1.0–2.0 mol % PPh<sub>3</sub>; 25 mmol; neat; 145 °C; 20 h. <sup>b</sup>Run to complete conversion. <sup>c</sup>GC yield.

Hexamethyldisilane was commercially available. 1,2-Dichlorotetramethyldisilane was obtained in large quantity (>5 gal) from methyl chloride and silicon direct-process streams. It could also be prepared in laboratory quantities from chlorodemethylation of hexamethyldisilane<sup>18</sup> or mercury-sensitized photolysis of dimethylchlorosilane.<sup>19</sup> The latter method is the recommended procedure for preparation of quantities less than 1 L. *sym*-Tetrachlorodimethyldisilane was available in large quantities by treatment of the direct-process disilane containing materials with HCl/aluminum chloride according to the procedure of Kumada et al.<sup>16</sup> Bis(benzonitrile)palladium chloride was prepared from palladium chloride and benzonitrile.<sup>20</sup>

Gas chromatographic analyses were carried out on a Shimadzu GC-9A instrument generally employing a 10 ft × 1/8 in. 20% SE30 on Chromasorb W 100/120-mesh analytical column. NMR data were recorded on a Varian EM 390 spectrometer. Infrared analysis was performed on a Perkin-Elmer 595 instrument.

**Palladium-Catalyzed Reactions of Aryl Acid Chlorides with Hexamethyldisilane.** Hexamethyldisilane was reacted with the following series of aromatic acid chlorides: benzoyl chloride, *p*-anisoyl chloride, *p*-chlorobenzoyl chloride, *p*-nitrobenzoyl chloride, *N*-*n*-butyltrimellitimide acid chloride, and trimellitic anhydride acid chloride. The reactions were carried out in a similar fashion to the catalysis between hexamethyldisilane and benzoyl chloride here described.

A mixture containing 100 mg (0.7 mmol) of benzoyl chloride and 200 mg (1.4 mmol) of hexamethyldisilane was heated neat to 125 °C to which was added 10 mg of bis(benzonitrile)palladium chloride and 18 mg of triphenylphosphine. Decane was added as an internal standard, and GC response factors for phenyltrimethylsilane and benzoyltrimethylsilane were determined from authentic samples.<sup>21</sup> The sample was heated to 125 °C for 24 h after which GC analysis showed the product composition to be 5% phenyltrimethylsilane, 79% benzoyltrimethylsilane, and 16% trimethylsilyl benzoate. Yields from other aryl acid chlorides investigated are shown in Table I.

Response factors for *p*-(trimethylsilyl)anisole and *p*-anisoyltrimethylsilane,<sup>22</sup> *p*-(trimethylsilyl)phenyl chloride and (*p*-chlorobenzoyl)-

trimethylsilane,<sup>10</sup> and (*p*-nitrophenyl)trimethylsilane and (*p*-nitrobenzoyl)trimethylsilane<sup>10</sup> were obtained from authentic samples prepared by previously described syntheses.

Product ratios and identities for the reactions of *N*-*n*-butyltrimellitimide acid chloride and trimellitic anhydride acid chloride were determined by GC-mass spectrometry: *N*-*n*-butyl-4-chlorophthalimide, 8%; *N*-*n*-butyl-4-(trimethylsilyl)phthalimide (**2e**), 42% (GCMS *m/e* 275, *p*<sup>+</sup>, 65% base peak; *m/e* 260, *p*<sup>+</sup> - CH<sub>3</sub>, 100% base peak; *m/e* 246, *p*<sup>+</sup> - C<sub>2</sub>H<sub>5</sub>, 10% base peak; *m/e* 232 *p*<sup>+</sup> - C<sub>3</sub>H<sub>7</sub>, 70% base peak; *m/e* 218, *p*<sup>+</sup> - C<sub>4</sub>H<sub>9</sub>, 10% base peak); and *N*-*n*-butyl-4-trimellitimidoyltrimethylsilane (**1e**), 49% (GCMS *m/e* 288, *p*<sup>+</sup> - CO, 25% base peak; *m/e* 73, Me<sub>3</sub>Si<sup>+</sup>, 100% base peak). 4-(Trimethylsilyl)phthalic anhydride (**2f**), 64% (GCMS *m/e* 220, *p*<sup>+</sup>, 10% base peak; *m/e* 205, *p*<sup>+</sup> - CH<sub>3</sub>, 100% base peak; *m/e* 176, *p*<sup>+</sup> - CO<sub>2</sub>, 10% base peak); 6% trimethylsilyl ester of trimellitic anhydride acid and 23% 4-trimellitoyltrimethylsilane (**1f**) (GCMS *m/e* 248, *p*<sup>+</sup>, 1% base peak; *m/e* 220, *p*<sup>+</sup> - CH<sub>3</sub>, 5% base peak; *m/e* 220, *p*<sup>+</sup> - CO, 35% base peak).

**Synthesis of Phenyl dimethylchlorosilane (3a).** A reaction mixture containing 2.93 g (2.1 × 10<sup>-2</sup> mol) of benzoyl chloride and 5 g (2.2 × 10<sup>-1</sup> mol) of 1,2-dichlorotetramethyldisilane was heated neat under an atmosphere of dry nitrogen at 140 °C. A catalyst mixture containing 8 mg (2.08 × 10<sup>-5</sup> mol, 1270 ppm) of bis(benzonitrile)palladium chloride and 11 mg (4.2 × 10<sup>-5</sup> mol, 2500 ppm) of triphenylphosphine was introduced, causing initiation of gaseous carbon monoxide evolution. The reaction was heated at 140 °C for 20 h. Following this period, distillation of the product mixture gave 2.46 g (91% yield) of dimethyldichlorosilane, bp 68–72 °C, and 3.12 g (87% yield) of phenyldimethylchlorosilane, bp 85 °C/20 Torr. A high-boiling fraction (160–175 °C/0.1 Torr) was recrystallized from pentane to give 0.2 g (9% yield) of benzil, mp 93–94 °C (lit. mp 94–95 °C).<sup>23</sup>

**Synthesis of *o*-Tolyldimethylchlorosilane (3b).** The reaction was carried out essentially as described for phenyldimethylchlorosilane. The following reagent proportions were employed: 5.0 g (3.24 × 10<sup>-2</sup> mol) of *o*-toluoyl chloride, 7.4 g (3.72 × 10<sup>-2</sup> mol) of 1,2-dichlorotetramethyldisilane, 25.0 mg (1800 ppm) of bis(benzonitrile)palladium chloride, and 32 mg (3600 ppm) of triphenylphosphine. After 15 h at 145 °C, gas chromatography analysis showed only 17% reaction of *o*-toluoyl chloride and 13% yield of *o*-tolyldimethylchlorosilane.

**Synthesis of *m*-Tolyldimethylchlorosilane (3c).** The reaction was essentially carried out as described for phenyldimethylchlorosilane. The following reagent amounts were employed: 5.0 g (3.24 × 10<sup>-2</sup> mol) of *m*-toluoyl chloride, 7.7 g (3.88 × 10<sup>-2</sup> mol) of 1,2-dichlorotetramethyldisilane, 25 mg (1800 ppm) of bis(benzonitrile)palladium chloride, and 33 mg (3600 ppm) of triphenylphosphine. After 15 h at 145 °C, distillation gave 4.88 g of a mixture of Me<sub>2</sub>SiCl<sub>2</sub> and excess ClMe<sub>2</sub>SiSiMe<sub>2</sub>Cl (84% mass balance) and 3.3 g of a material with a boiling point of 86 °C (13 Torr) which was shown by NMR and GC analyses to be an 85/15 mixture of *m*-tolyldimethylchlorosilane and 15% *m*-chlorotoluene, lit. bp 101–110 °C/20 Torr.<sup>25</sup> For *m*-toluoyldimethylchlorosilane: NMR (CCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub> reference) δ 7.1–7.5 (m, 4 H, aromatic), 2.41 (s, 3 H, benzylic), 0.69 (s, 6 H, SiMe<sub>2</sub>Cl). Following distillation, 2.1 g of pot residue was dissolved in hot isooctane, filtered, cooled, and refiltered, and the material was recrystallized from hexane to give 1.5 g of 3,3'-dimethylbenzil, mp 99–100 °C (lit. mp 102 °C).<sup>23</sup> Calcd for C<sub>16</sub>H<sub>14</sub>O<sub>2</sub> 238.0994; obsd 238.0991. Net conversion after 15 h at 145 °C was 100%. Product yields were 49% *m*-toluoyl chloride, 38% 3,3'-dimethylbenzil, and 2% *m*-chlorotoluene.

**Synthesis of *p*-Tolyldimethylchlorosilane (3d).** The reaction conditions were essentially identical with those described for phenyldimethylchlorosilane. The following reagent amounts were employed: 5.0 g (3.23 × 10<sup>-2</sup> mol) of *p*-toluoyl chloride, 6.42 g (3.23 × 10<sup>-2</sup> mol) of 1,2-dichlorotetramethyldisilane, 25 mg (1800 ppm) of bis(benzonitrile)palladium chloride, and 30 mg (3600 ppm) of triphenylphosphine. After 15 h at 145 °C, distillation gave 4.7 g of a mixture of Me<sub>2</sub>SiCl<sub>2</sub> and residual ClMe<sub>2</sub>SiSiMe<sub>2</sub>Cl, bp 65–140 °C, and 2.93 g (49% isolated yield) of *p*-tolyldimethylchlorosilane, bp 87 °C/12 Torr (lit. bp 107–117 °C/25 Torr).<sup>24</sup> For *p*-tolyldimethylchlorosilane: NMR (CCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub> reference): δ 7.35 and 7.15 (AA',BB', 4 H, *J* = 8.5 Hz, aromatic), 2.35 (s, 3 H, benzylic), 0.65 (s, 6 H, SiMe<sub>2</sub>Cl). Following distillation, 2.46 g of pot residue material remained, which was dissolved in hot isooctane, hot filtered, cooled, filtered, and recrystallized from hexane to give 4,4'-dimethylbenzil as yellow crystals, mp 102–103 °C (lit. mp 104 °C).<sup>23</sup>

**Synthesis of (*o*-Chlorophenyl)dimethylchlorosilane (3e).** The reaction conditions were essentially identical with those described for phenyldi-

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methylchlorosilane. The following reagent amounts were employed: 5 g ( $2.86 \times 10^{-2}$  mol) of *o*-chlorobenzoyl chloride, 7 g ( $3.84 \times 10^{-2}$  mol) of 1,2-dichlorotetramethyldisilane, 20 mg (1800 ppm) of bis(benzonitrile)palladium chloride, and 30 mg (3600 ppm) of triphenylphosphine. The reaction was slower than the corresponding para or meta examples. After 15 h at 145 °C, distillation gave 3.0 g of a material boiling at 100–110 °C/10 Torr, which was shown by GC and NMR analyses to be a 2/1 mixture of unreacted *o*-chlorobenzoyl chloride and product, (*o*-chlorophenyl)dimethylchlorosilane. High-resolution GCMS further confirmed the product structure: calcd  $C_8H_{10}Si^{37}Cl^{37}Cl$  207.9869, obsd 297.9857, int = 7.98% base; calcd  $C_8H_{10}Si^{37}Cl^{35}Cl$  205.9899, obsd 205.9869, int = 41.82% base; calcd  $C_8H_{10}Si^{35}Cl^{35}Cl$  203.9929, obsd 203.9826, int = 598.59% base. NMR for (*o*-chlorophenyl)dimethylchlorosilane ( $CCl_4$ ,  $CH_2Cl_2$  reference):  $\delta$  7.1–7.4 (m, 4 H, aromatic), 0.70 (s, 6 H,  $SiMe_2Cl$ ). After 15 h at 145 °C conversion was 50%; net isolated yield of (*o*-chlorophenyl)dimethylchlorosilane was 25%.

**Synthesis of (*m*-Chlorophenyl)dimethylchlorosilane (3f).** A reaction mixture containing 5 g ( $2.86 \times 10^{-2}$  mol) of *m*-chlorobenzoyl chloride and 6.8 g ( $3.4 \times 10^{-2}$  mol) of 1,2-dichlorotetramethyldisilane was heated neat to 140 °C under an atmosphere of dry nitrogen. A catalyst mixture containing 20 mg (1800 ppm) of bis(benzonitrile)palladium chloride and 27 mg (3600 ppm) of triphenylphosphine was added and the reaction heated to 145 °C for 15 h during which time carbon monoxide evolved from the reaction. Distillation gave 4.7 g of a mixture of  $Me_2SiCl_2$  and excess unreacted  $ClMe_2SiSiMe_2Cl$ , bp 65–140 °C. Vacuum distillation gave 4.4 g of material with a boiling point of 105–110 °C/10 Torr, which was shown by NMR and GC analysis to be an 80/20 mixture of (*m*-chlorophenyl)dimethylchlorosilane and unreacted starting material. Net conversion in 15 h/145 °C was 83%; 73% isolated yield of (*m*-chlorophenyl)dimethylchlorosilane, lit. bp 108–120 °C/16 Torr.<sup>24</sup> For (*m*-chlorophenyl)dimethylchlorosilane: NMR ( $CCl_4$ ,  $CH_2Cl_2$  reference)  $\delta$  7.1–7.45 (m, 3 H, aromatic), 0.60 (s, 6 H,  $SiMe_2Cl$ ); IR (neat film) 3060, 2980  $cm^{-1}$ .

**Synthesis of (*p*-Chlorophenyl)dimethylchlorosilane (3g).** A reaction mixture containing 3.64 g ( $2.1 \times 10^{-2}$  mol) of *p*-chlorobenzoyl chloride and 5.0 g ( $2.2 \times 10^{-2}$  mol) of 1,2-dichlorotetramethyldisilane was heated to 140 °C under an atmosphere of nitrogen. A catalyst mixture containing 8 mg (0.1 mol %) of bis(benzonitrile)palladium chloride and 11 mg (0.2 mol %) of triphenylphosphine was added, and the reaction was heated at 140 °C for 20 h. Fractional distillation gave 3.7 g of (*p*-chlorophenyl)dimethylchlorosilane, bp 220–114 °C/11 Torr (lit. bp 103 °C/12 Torr and 106–109 °C/18 Torr).<sup>25</sup> *o*-Dichlorobenzene was observed as a side product (1.5%) as well as several smaller volatile components.

**Synthesis of *o*-Anisyldimethylchlorosilane (3h).** The experiment was carried out essentially as described for phenyldimethylchlorosilane. The following proportion of reagents was employed: 5 g ( $2.93 \times 10^{-2}$  mol) of *m*-anisoyl chloride, 7.0 g ( $3.5 \times 10^{-2}$  mol) of 1,2-dichlorotetramethyldisilane, 20 mg (1800 ppm) of bis(benzonitrile)palladium chloride, and 28 mg (3600 ppm) of triphenylphosphine. After 15 h at 145 °C, distillation gave 2.95 g of volatile chlorosilanes  $Me_2SiCl_2$  and excess  $ClMe_2SiSiMe_2Cl$ , bp 65–140 °C, 0.75 g (18% isolated yield) of *o*-chloroanisole, bp 80–90 °C/25 Torr, and 1.75 g (32% isolated yield) of *o*-anisyldimethylchlorosilane, bp 110 °C/8 mmHg; 1.18 g of nonvolatile residue material was isolated. For *o*-anisyldimethylchlorosilane: NMR ( $CCl_4$ ,  $CH_2Cl_2$  reference)  $\delta$  7.50 (d of d, 1 H,  $J_{3,4} = 7.2$  Hz,  $J_{3,5} = 1.3$  Hz, aromatic H<sub>3</sub>), 7.26 (d of d of d, 1 H,  $J_{5,6} = 8.4$  Hz,  $J_{4,5} = 7.2$  Hz,  $J_{3,5} = 1.3$  Hz, aromatic H<sub>5</sub>), 6.90 (td, 1 H,  $J_{3,4} = J_{4,5} = 7.2$  Hz,  $J_{4,6} = 0.9$  Hz, aromatic H<sub>6</sub>), 6.70 (d of d, 1 H,  $J_{5,6} = 8.4$  Hz,  $J_{4,6} = 0.9$  Hz, aromatic H<sub>6</sub>), 3.70 (s, 3 H, OCH<sub>3</sub>), 0.60 (s, 6 H,  $SiMe_2Cl$ ).

**Synthesis of *m*-Anisyldimethylchlorosilane (3i).** The experiment was carried out essentially as described for phenyldimethylchlorosilane. The following proportion of reagents was employed: 5.0 g ( $2.93 \times 10^{-2}$  mol) of *m*-anisoyl chloride, 7 g ( $3.5 \times 10^{-2}$  mol) of 1,2-dichlorotetramethyldisilane, 20 mg (1800 ppm) of bis(benzonitrile)palladium dichloride, and 28 mg (3600 ppm) of triphenylphosphine. After 15 h at 145 °C, distillation gave 3.33 g (89% yield) of  $Me_2SiCl_2$ , bp 65–74 °C, and 2.76 g (47% isolated yield) of *m*-anisyldimethylchlorosilane, bp 90 °C/4 mmHg; 8% unreacted *m*-anisoyl chloride was also obtained. Gas chromatography analysis showed 2% formation of *m*-chloroanisole; 1.3 g of nonvolatile residue material remained after distillation. For *m*-anisyldimethylchlorosilane: NMR ( $CCl_4$ ,  $CH_2Cl_2$  reference)  $\delta$  6.8–7.4 (m, 4 H, aromatic), 3.80 (s, 3 H, OMe), 0.72 (s, 6 H,  $SiMe_2Cl$ ).

**Synthesis of *p*-Anisyldimethylchlorosilane (3j).** The procedure was carried out similar to that described for phenyldimethylchlorosilane. The following proportion of reagents was employed: *p*-anisyl chloride, 3.55 g ( $2.1 \times 10^{-2}$  mol); 1,2-dichlorotetramethyldisilane, 5 g ( $2.2 \times 10^{-2}$  mol); bis(benzonitrile)palladium chloride, 8 mg (0.1 mol %); and triphenylphosphine, 11 mg (0.2 mol %). After reaction at 140 °C for 20 h, fractional distillation gave 0.48 g (15%) of *p*-chloroanisole, bp 77 °C/15

Torr, and 2.19 g (52% isolated yield) of *p*-anisyldimethylchlorosilane, bp 101–105 °C/10 Torr (lit. bp 126–124 °C/16 Torr).<sup>26</sup>

**Synthesis of (*m*-Nitrophenyl)dimethylchlorosilane (3k).** The experiment was carried out essentially as described for phenyldimethylchlorosilane. The following proportion of reagents was employed: 5 g ( $2.7 \times 10^{-2}$  mol) of *m*-nitrobenzoyl chloride, 7 g ( $3.5 \times 10^{-2}$  mol) of 1,2-dichlorotetramethyldisilane, 22 mg (1800 ppm) of bis(benzonitrile)palladium dichloride, and 29 mg (3600 ppm) of triphenylphosphine. After 15 h at 145 °C, distillation gave 3.4 g of  $Me_2SiCl_2$  and 1.6 g of recovered excess  $ClMe_2SiSiMe_2Cl$  (80% mass balance). Vacuum distillation gave 4.32 g of (*m*-nitrophenyl)dimethylchlorosilane (74% isolated yield), bp 112 °C/1 Torr. For (*m*-nitrophenyl)dimethylchlorosilane: NMR ( $CCl_4$ ,  $CH_2Cl_2$  reference)  $\delta$  8.25 (d of d of d, 1 H,  $J_{2,4} = 2.6$  Hz,  $J_{2,5} = 1.3$  Hz,  $J_{2,6} = 1.3$  Hz, aromatic H<sub>2</sub>), 8.05 (d of d of d, 1 H,  $J_{2,4} = 2.6$  Hz,  $J_{4,5} = 8.4$  Hz,  $J_{4,6} = 1.3$  Hz, aromatic H<sub>4</sub>), 7.70 (d of t, 1 H,  $J_{2,6} = J_{4,6} = 1.3$  Hz,  $J_{5,6} = 8.4$  Hz, aromatic H<sub>6</sub>), 7.45 (t of d, 1 H,  $J_{4,5} = J_{5,6} = 8.4$  Hz,  $J_{1,4} = 1.3$  Hz, aromatic H<sub>3</sub>), 0.67 (s, 6 H,  $SiMe_2Cl$ ).

**Synthesis of (*p*-Nitrophenyl)dimethylchlorosilane (3l).** The experiment was carried out as described for phenyldimethylchlorosilane. The following proportion of reagents was employed: 3.86 g ( $2.1 \times 10^{-2}$  mol) of *p*-nitrobenzoyl chloride, 5.0 g ( $2.2 \times 10^{-2}$  mol) of 1,2-dichlorotetramethyldisilane, 8 mg (0.1 mol %) of bis(benzonitrile)palladium chloride, and 11 mg (0.2 mol %) of triphenylphosphine. Vacuum distillation gave 3.25 g (72% isolated yield) of (*p*-nitrophenyl)dimethylchlorosilane, bp 110 °C/1 Torr.

**Synthesis of (*p*-Cyanophenyl)dimethylchlorosilane (3m).** *p*-Cyanobenzoyl chloride was sublimed prior to use to separate it from residual *p*-cyanobenzoic acid. A reaction mixture containing 10 g ( $6.0 \times 10^{-2}$  mol) of *p*-cyanobenzoyl chloride and 15 g (1.25 mol equiv) of 1,2-dichlorotetramethyldisilane was heated to 145 °C neat under an atmosphere of dry nitrogen. At that point a catalyst mixture containing 200 mg ( $5.22 \times 10^{-4}$  mol, 0.9 mol %) of bis(benzonitrile)palladium chloride and 274 mg ( $1.04 \times 10^{-3}$  mol, 2 mol %) of triphenylphosphine was introduced, causing evolution of carbon monoxide from the system. Dimethyldichlorosilane was removed continuously from the reaction mixture, and after 15 h at 145 °C, a quantitative yield was obtained. Vacuum distillation of the remaining material gave 7.0 g (60% isolated yield) of (*p*-cyanophenyl)dimethylchlorosilane, bp 93 °C/0.2 Torr. This material could be recrystallized from dry pentane to give colorless crystals, mp 40–43 °C. The product was extremely hygroscopic and was best stored cold. For (*p*-cyanophenyl)dimethylchlorosilane: NMR ( $CCl_4$ ,  $CH_2Cl_2$  reference)  $\delta$  7.63 and 7.50 (AA'BB', 4 H,  $J \approx 8$  Hz, aromatic), 0.60 (s, 6 H,  $SiMe_2Cl$ ).

**Synthesis of *o*-(Chlorodimethylsilyl)benzoyl Chloride (3n).** A reaction mixture containing 5 g ( $3.24 \times 10^{-2}$  mol) of phthaloyl chloride and 7.4 g ( $3.7 \times 10^{-2}$  mol) of 1,2-dichlorotetramethyldisilane was heated neat to 145 °C under an atmosphere of nitrogen. A catalyst mixture containing 25 mg of bis(benzonitrile)palladium chloride and 33 mg of triphenylphosphine was introduced. A slow reaction ensued, and after 15 h at 145 °C, GC analysis showed the following mixture composition: 18% *o*-chlorobenzoyl chloride, 56% unreacted phthaloyl chloride, and 19% 2-(chlorodimethylsilyl)benzoyl chloride. Three unidentified materials were formed in yields of <4% each.

**Synthesis of *m*-(Chlorodimethylsilyl)benzoyl Chloride (3o).** A reaction mixture containing 5.0 g ( $3.24 \times 10^{-2}$  mol) of isophthaloyl chloride and 7.4 g ( $3.7 \times 10^{-2}$  mol) of 1,2-dichlorotetramethyldisilane was heated neat to 145 °C under an atmosphere of dry nitrogen. A catalyst mixture containing 25 mg of bis(benzonitrile)palladium chloride and 32 mg of triphenylphosphine was introduced, initiating CO evolution from the reaction. After 15 h at 145 °C, gaseous expulsion ceased, and fractional distillation gave 3.7 g (61% isolated yield) of *m*-(chlorodimethylsilyl)benzoyl chloride, bp 127 °C/2 Torr, as a pale yellow liquid. Careful redistillation showed pure material to be a colorless liquid; 0.57 g of high-boiling pot residue was also isolated. For *m*-(chlorodimethylsilyl)benzoyl chloride: NMR ( $CCl_4$ ,  $CH_2Cl_2$  reference)  $\delta$  8.23 [br s (d of d unresolved), 1 H, H<sub>2</sub>], 8.03 (d of d, 1 H,  $J_{4,5} = 7.5$  Hz,  $J_{4,6} = 2$  Hz, H<sub>4</sub>), 7.45 (s, 1 H,  $J_{4,5} = J_{5,6} = 7.5$  Hz, H<sub>3</sub>), 7.83 (d of d,  $J_{4,6} = 2$  Hz,  $J_{5,6} = 7.5$  Hz, H<sub>6</sub>), 0.75 (s, 6 H,  $SiMe_2Cl$ ); infrared (neat film) 1760  $cm^{-1}$  (s, COCl); mass spectrum  $m/e$  232,  $p^+$ , base peak.

**Synthesis of *p*-(Chlorodimethylsilyl)benzoyl Chloride (3p).** A reaction mixture containing 304.5 g (1.5 mol) of terephthaloyl chloride and 350 g (1.75 mol) of 1,2-dichlorotetramethyldisilane was heated neat to 145 °C under an atmosphere of nitrogen. When the mixture became homogeneous, a catalyst mixture containing 0.5 g ( $1.29 \times 10^{-3}$  mol, 860 ppm) of bis(benzonitrile)palladium chloride and 0.6 g ( $2.3 \times 10^{-3}$  mol, 1500 ppm) of triphenylphosphine was introduced, causing initiation of

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gaseous carbon monoxide evolution. After 24 h at 145 °C, distillation gave 370 g (96% yield) of dimethyldichlorosilane, bp 65–70 °C, and 275 g (77% isolated yield) of 4-(chlorodimethylsilyl)benzoyl chloride, bp 89 °C/1 Torr (lit. bp 104 °C/8 Torr).<sup>28</sup> For *p*-(chlorodimethylsilyl)benzoyl chloride: NMR (CCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub> reference) δ 7.95 and 7.68 (AA'BB', 4 H, *J* = 9 Hz, aromatic), 0.6 (s, 6 H, SiMe<sub>2</sub>Cl); infrared (neat film) 1778 (s), 1742 (vs, COCl), 1595 (m), 1390 cm<sup>-1</sup> (m).

**Synthesis of 1,3-Bis(chlorodimethylsilyl)benzene (3q).** A reaction mixture containing 5.0 g (2.46 × 10<sup>-2</sup> mol) of isophthaloyl chloride and 12.4 g (6.63 × 10<sup>-2</sup> mol) of 1,2-dichlorotetramethyldisilane was heated neat to 145 °C under an atmosphere of dry nitrogen. A cocatalyst mixture containing 40 mg of bis(benzonitrile)palladium chloride and 54 mg of triphenylphosphine was then introduced, causing evolution of carbon monoxide gas. The reaction mixture was heated to 145 °C for 60 h following which the product mixture was fractionally distilled to give 5 g of dimethyldichlorosilane, bp 67–72 °C, and 4.2 g (66% isolated yield) of 1,3-bis(chlorodimethylsilyl)benzene (bp 113 °C/2 Torr) as a colorless liquid. For 1,3-bis(chlorodimethylsilyl)benzene: NMR (CCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub> reference) δ 7.3–7.9 (m, 4 H, aromatic), 0.72 (s, 12 H, SiMe<sub>2</sub>Cl); IR (neat film) 2970 (w, C–H), 1261 cm<sup>-1</sup> (m, Si–C); mass spectrum 262, *p*<sup>+</sup>; bp 200 °C.

**Synthesis of 1,4-Bis(chlorodimethylsilyl)benzene (3r).** A 1-L three-neck flask was equipped with a mechanical stirrer and a 36-in. vigreux column with an attached distillation apparatus. A reaction mixture containing 100 g (0.49 mol) of terephthaloyl chloride and 200 g (1.01 mol) of 1,2-dichlorotetramethyldisilane was introduced and heated to 145 °C under an atmosphere of dry nitrogen. When the solution became homogeneous, a catalyst mixture containing 150 mg (3.9 × 10<sup>-4</sup> mol, 880 ppm) of bis(benzonitrile)palladium chloride and 20 mg (7.8 × 10<sup>-4</sup> mol, 1600 ppm) of triphenylphosphine was introduced. The reaction temperature was maintained at 145 °C for 24 h during which CO evolved and approximately 1 mol of Me<sub>2</sub>SiCl<sub>2</sub> was removed. The reaction temperature was then increased to 175 °C and maintained for an additional 48 h. After 72-h reaction time the material was fractionally distilled to give 72 g (55% isolated yield) of 1,4-bis(chlorodimethylsilyl)benzene, bp 130 °C/1 Torr (lit. bp 150–155 °C/19 Torr).<sup>28</sup> The material could be further purified by recrystallization from pentane to give 57 g of crystalline material, mp 86–87 °C, (lit. mp 87 °C);<sup>28</sup> NMR (CCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub> reference) δ 7.58 (s, 4 H, aromatic), 0.6 (s, 12 H, SiMe<sub>2</sub>Cl).

**Synthesis of 4-(Chlorodimethylsilyl)phthalic Anhydride (3s).** A 5-L three-neck flask was equipped with a mechanical stirrer, 250-mL dropping funnel, and a 24-in. vigreux column with an attached distillation head. A reaction mixture containing 1500 g (7.13 mol) of trimellitic anhydride acid chloride and 1490 g (7.48 mol) of 1,2-dichlorotetramethyldisilane was added and stirred neat at 145 °C under an atmosphere of nitrogen. When the mixture became homogeneous, 1.65 g (4.3 × 10<sup>-3</sup> mol, 600 ppm) of bis(benzonitrile)palladium chloride and 2.24 g (8.54 × 10<sup>-3</sup> mol, 1200 ppm) of triphenylphosphine were introduced. Vigorous evolution of carbon monoxide gas ensued with an accompanying exothermic reaction. The external heat was decreased to maintain a constant reaction temperature between 140 and 150 °C. As dimethyldichlorosilane was formed, it was continuously removed from the reaction mixture, bp 69–70 °C. After 15 h at 145–150 °C, evolution of gas ceased, and gas chromatographic analysis showed 93% conversion to 4-(chlorodimethylsilyl)phthalic anhydride. The crude sample also contained a considerable amount of dimethyldichlorosilane, which was removed under reduced pressure and condensed in a dry ice/acetone trap. Net yield of volatile chlorosilanes Me<sub>2</sub>SiCl<sub>2</sub>, and excess ClMe<sub>2</sub>SiSiMe<sub>2</sub>Cl was 956.6 g (97% mass balance). The product could be isolated by vacuum distillation as a colorless, slightly viscous liquid, bp 143 °C/1 Torr; NMR (CCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub> reference) δ 7.98 (s, 1 H, aromatic H<sub>3</sub>), 7.94 (d, 1 H, *J*<sub>5,6</sub> = 7.5 Hz, aromatic H<sub>6</sub>), 7.77 (d, 1 H, *J*<sub>5,6</sub> = 7.5 Hz, aromatic H<sub>5</sub>), 0.65 (s, 6 H, SiMe<sub>2</sub>Cl); IR (neat film) 1850, 1775 cm<sup>-1</sup> (anhydride); mass spectrum calcd 240.0008, obsd 240.0016, error 3.3 ppm.

**Synthesis of 4-(Dichloromethylsilyl)phthalic Anhydride.** A reaction mixture containing 50 g (0.24 mol) of trimellitic anhydride acid chloride and 54 g (0.24 mol) of *sym*-tetrachlorodimethyldisilane was heated neat to 145 °C under an atmosphere of dry nitrogen. When the mixture was homogeneous, 1.1 × 10<sup>-3</sup> mol of palladium catalyst and 2.2 × 10<sup>-3</sup> mol of phosphine cocatalyst were introduced, initiating carbon monoxide evolution from the system. Methyltrichlorosilane, bp 68 °C, was removed continuously as it formed, and after 24-h reaction time, 18.7 g (52% isolated yield) of MeSiCl<sub>3</sub> had been obtained. The mixture was cooled and the catalyst removed by filtration. Fractional distillation gave 39.5 g (63% yield) 4-(dichloromethylsilyl)phthalic anhydride as a colorless, viscous oil, bp 124 °C/0.05 Torr; NMR (CDCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> reference) δ 8.35 (br s, 1 H, H<sub>3</sub>), 8.28 (s, 1 H, *J*<sub>5,6</sub> = 8 Hz, H<sub>6</sub>), 8.08 (d, 1 H, *J*<sub>5,6</sub> = 8 Hz, H<sub>5</sub>), 1.10 (s, 3 H, SiMeCl<sub>2</sub>); infrared (neat film) 1845 (s), 1770

cm<sup>-1</sup> (vs) (acid anhydride); mass spectrum, calcd for C<sub>9</sub>H<sub>6</sub>O<sub>3</sub>Si<sup>35</sup>Cl<sub>2</sub> 259.9463, obsd. 259.9464, error 0.1 ppm.

**Synthesis of *N*-Methyl-4-(dichloromethylsilyl)phthalimide.** A reaction mixture containing 98 g (0.43 mol) of *N*-methyltrimellitimide acid chloride and 100 g (0.44 mol) of *sym*-tetrachlorodisilane was heated neat to 145 °C under nitrogen. When the mixture was homogeneous, 1 × 10<sup>-3</sup> mol of palladium catalyst and 2 × 10<sup>-3</sup> mol of phosphine cocatalyst were introduced, initiating evolution of CO gas. After 24 h at 145 °C, 61 g of methyltrichlorosilane was obtained (90% theoretical). Vacuum distillation gave 19 g (15% yield) of *N*-methyl-4-(dichloromethylsilyl)phthalimide, bp 155–65 °C/0.5 Torr, which crystallized upon cooling. The product could be further purified by vacuum sublimation (100 °C/0.1 Torr) to give colorless hygroscopic crystals, mp 89–95 °C; NMR δ 8.05 (br s, 1 H, aromatic H<sub>3</sub>), 7.98 (d, H, *J* = 8 Hz, aromatic H<sub>6</sub>), 7.75 (d, 1 H, *J* = 8 Hz, aromatic H<sub>5</sub>), 3.1 (s, 3 H, N–CH<sub>3</sub>), 1.1 (s, 3 H, Si–CH<sub>3</sub>); IR (Nujol) 1757, 1703 cm<sup>-1</sup> (s, imide carbonyl); mass spectrum, calcd 272.9779, obsd 272.9776.

**Synthesis of (*m*-Nitrophenyl)dichloromethylsilane.** A reaction mixture containing 50 g (2.69 × 10<sup>-1</sup> mol) of *m*-nitrobenzoyl chloride and 61.5 g (2.69 × 10<sup>-1</sup> mol) of *sym*-tetrachlorodimethyldisilane was heated neat to 140 °C under nitrogen to which was added 1 mol % palladium catalyst and 2 mol % phosphine cocatalyst. Gaseous evolution of carbon monoxide ensued, and after 13 h at 140 °C, 26.7 g of methyltrichlorosilane was isolated. Vacuum distillation of the remaining material gave 43.9 g (69% isolated yield) of (*m*-nitrophenyl)dichloromethylsilane, bp 119 °C/1 Torr; NMR (CCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub> reference) δ 8.75 (d, d, d, 1 H, *J*<sub>2,4</sub> = 2.6 Hz, *J*<sub>2,5</sub> = 1.3 Hz, *J*<sub>2,6</sub> = 1.3 Hz, aromatic H<sub>2</sub>), 8.55 (d, d, d, 1 H, *J*<sub>2,4</sub> = 2.6 Hz, *J*<sub>4,5</sub> = 8.4 Hz, *J*<sub>4,6</sub> = 1.3 Hz, aromatic H<sub>4</sub>), 8.20 (d, t, 1 H, *J*<sub>2,6</sub> = *J*<sub>4,6</sub> = 1.3 Hz, *J*<sub>5,6</sub> = 8.4 Hz, aromatic H<sub>6</sub>), 7.95 (t, d, 1 H, *J*<sub>4,5</sub> = *J*<sub>5,6</sub> = 8.4 Hz, *J*<sub>1,4</sub> = 1.3 Hz, aromatic H<sub>5</sub>), 0.91 (s, 3 H, SiCH<sub>3</sub>Cl<sub>2</sub>); IR (thin film) 1601 (C=C aromatic), 1520, 1345 cm<sup>-1</sup> (NO<sub>2</sub>); mass spectrum calcd 234.9623; obsd 234.9618, error 2 ppm.

**Synthesis of *p*-(Dichloromethylsilyl)benzoyl Chloride.** A reaction mixture containing 100 g (0.49 mol) of terephthaloyl chloride and 116 g (0.51 mol) of *sym*-tetrachlorodimethyldisilane was heated to 145 °C under an atmosphere of dry nitrogen. After the solution became homogeneous 0.3 mol % palladium catalyst and 0.6 mol % phosphine cocatalyst were introduced, which initiated carbon monoxide evolution. As MeSiCl<sub>3</sub> formed, it was removed continuously by distillation, bp 68–71 °C. After 24 h at 145 °C, the heating was ceased, and 65 g (89% isolated yield) of Cl<sub>2</sub>SiMe<sub>2</sub> was removed during the reaction. Fractional distillation gave 74.4 g (60% isolated yield) of *p*-(dichloromethylsilyl)benzoyl chloride, bp 126 °C/3 Torr, as a clear colorless liquid; NMR (CCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub> reference) δ 7.96 and 7.70 (AA'BB', 4 H, *J* = 8 Hz, aromatic), 0.95 (s, 3 H, SiMeCl<sub>2</sub>); infrared (neat film) 1780, 1743 (s, COCl), 1391 (s, C–H bend), 1257 cm<sup>-1</sup> (m, Si–C stretch).

**Synthesis of (*p*-Cyanophenyl)dichloromethylsilane.** A reaction mixture containing 17.1 g (0.10 mol) of *p*-cyanobenzoyl chloride and 23.5 g (1.10 mol) of *sym*-tetrachlorodimethyldisilane was heated neat to 140 °C to which was added 1 × 10<sup>-3</sup> mol of palladium catalyst and 2 × 10<sup>-3</sup> mol of phosphine cocatalyst. Gaseous carbon monoxide evolved, and after 12 h at 140 °C, 12.5 g (81% yield) of methyltrichlorosilane (bp 67 °C) was isolated. Vacuum distillation gave 5.65 g (25% isolated yield) of (*p*-cyanophenyl)dichloromethylsilane, bp 90 °C/0.1 Torr, which crystallized upon cooling. The material could be recrystallized from hexane to give extremely hygroscopic colorless crystals; NMR (CCl<sub>4</sub>, TMS reference) δ 7.72 (AA'BB' q, 4 H, *J* ≈ 9.14 Hz), 1.03 (s, 3 H, SiCH<sub>3</sub>Cl<sub>2</sub>); IR (Nujol mull) 2220 cm<sup>-1</sup> (CN); mass spectrum, calcd 214.9725, obsd 214.9725.

**Reaction of Pivaloyl Chloride with 1,2-Dichlorotetramethyldisilane.** A reaction mixture containing 5.0 g (4.15 × 10<sup>-2</sup> mol) of pivaloyl chloride and 12.4 g (6.6 × 10<sup>-2</sup> mol) of 1,2-dichlorotetramethyldisilane was dissolved in 50 mL of dry diglyme. A solvent was employed because of the volatility of pivaloyl chloride. A catalytic amount of bis(benzonitrile)palladium chloride and triphenylphosphine was added and the mixture heated to 145 °C for 15 h during which time gas evolved from the reaction. Fractional distillation gave a quantitative recovery of unreacted disilane.

The experiment was reinvestigated by utilizing 41 mg (3.4 × 10<sup>-4</sup> mol) of pivaloyl chloride and 1.5 g (25-fold excess) of 1,2-dichlorotetramethyldisilane. The volume of gas evolved was carefully monitored with a gas buret. When gaseous evolution ceased, 21.4 mL (2.7 mol equiv) of gas displacement had occurred. Analysis of the gas by IR confirmed the presence of HCl and CO. GC analysis confirmed the formation of isobutylene.

**Reaction of Cyclohexanecarboxylic Acid Chloride with Palladium Catalyst in the Presence of 1,2-Dichlorotetramethyldisilane.** A reaction mixture containing 50 g (3.41 × 10<sup>-2</sup> mol) cyclohexanecarboxylic acid chloride, 8.14 g (4.36 mol) of 1,2-dichlorotetramethyldisilane, 25 mg (6.35 × 10<sup>-5</sup> mol) of bis(benzonitrile)palladium chloride, and 33 mg (1.26



$\times 10^{-4}$  mol) of triphenylphosphine was heated to 145 °C for 15 h. Distillation of the product mixture gave 4.3 g (82% yield) of cyclohexene and recovery of 1,2-dichlorotetramethyldisilane unreacted.

**Reaction of Diphenic Acid Chloride with 1,2-Dichlorotetramethyldisilane.** A reaction mixture containing 5.0 g ( $1.79 \times 10^{-2}$  mol) of diphenic acid chloride and 7.13 g ( $3.58 \times 10^{-2}$  mol) of 1,2-dichlorotetramethyldisilane was heated to 145 °C, neat, under an atmosphere of nitrogen. A catalyst mixture comprising 25 mg of bis(benzonitrile)palladium chloride and 33 mg of triphenylphosphine was introduced, initiating rapid evolution of carbon monoxide from the mixture. After 15 h at 145 °C,

gaseous evolution had ceased, and distillation gave 2.1 g of  $\text{Me}_2\text{SiCl}_2$ , bp 68–71 °C, and 3.5 g of unreacted 1,2-dichlorotetramethyldisilane, bp 144–148 °C. Vacuum distillation at 145 °C/1 Torr gave a yellow-orange material which was recrystallized from hexane/toluene to give 3.12 g (97% yield) of fluorenone, mp 78–82 °C (lit. mp 83–85 °C).<sup>29</sup> The structure was further confirmed by high-resolution mass spectroscopy.

(29) *Handbook of Chemistry and Physics*, 48th ed.; Weast, R. C., Ed.; Chemical Rubber Co.: Cleveland, 1967; p C-325.

## Kinetics of Hydrolysis of Substituted $\beta$ -Nitrostyrenes. Transition-State Imbalances and Intrinsic Rate Constants for Three Different Types of Nitronate Ion Forming Processes. Relevance to the Nitroalkane Anomaly<sup>1</sup>

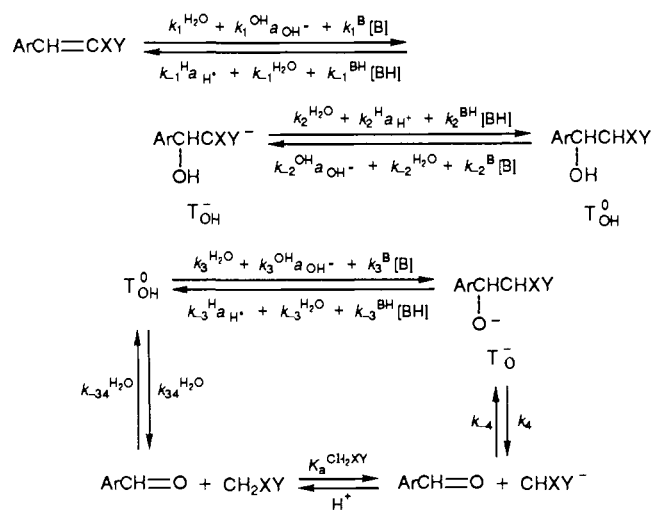
Claude F. Bernasconi\* and Peter Paschalis

Contribution from the Thimann Laboratories of the University of California, Santa Cruz, California 95064. Received January 9, 1989

**Abstract:** A kinetic study of the hydrolysis of  $\beta$ -nitrostyrene and of the 4-chloro and 3-nitro derivatives in 50%  $\text{Me}_2\text{SO}$ -50% water (v/v) at 20 °C is reported. The mechanism involves four steps: nucleophilic addition of  $\text{OH}^-$  or water to form  $\text{ArCH}(\text{OH})\text{CHNO}_2^-$  ( $\text{T}_{\text{OH}}^-$ ); carbon protonation of  $\text{T}_{\text{OH}}^-$  by water,  $\text{H}^+$ , and buffer acids to form  $\text{ArCH}(\text{OH})\text{CH}_2\text{NO}_2$  ( $\text{T}_{\text{OH}}^0$ ); deprotonation of the OH group in  $\text{T}_{\text{OH}}^0$  to form  $\text{ArCH}(\text{O}^-)\text{CH}_2\text{NO}_2$  ( $\text{T}_0^-$ ); collapse of  $\text{T}_0^-$  into  $\text{ArCHO}$  and  $\text{CH}_2\text{NO}_2^-$ . In strongly acidic solution the aci form of  $\text{T}_{\text{OH}}^0$ ,  $\text{PhCH}(\text{OH})\text{CH}=\text{NO}_2\text{H}$  ( $\text{T}_{\text{OH,aci}}^0$ ), which is generated by protonation of  $\text{T}_{\text{OH}}^-$  on the nitro group, could also be detected. All steps are reversible, and the rate and equilibrium constants of most of them could be determined by a combination of kinetic experiments starting with the substrate, the products, the independently synthesized  $\text{T}_{\text{OH}}^-$ , and  $\text{T}_{\text{OH}}^0$  (generated at high pH and then subjected to a pH jump) and by measuring product ratios spectrophotometrically or by HPLC analysis. The intrinsic rate constants of the proton transfer,  $\text{T}_{\text{OH}}^- \rightleftharpoons \text{T}_{\text{OH}}^0$ , are close to those for the deprotonation of nitromethane and 2-nitroethanol, and the Brønsted coefficients show a transition-state imbalance ( $\alpha_{\text{CH}} \gg \beta_{\text{B}^-}$ ) that is typical for the deprotonation of nitroalkanes. The other two processes that lead to the formation of a nitronate ion, i.e., nucleophilic addition to the olefin to form  $\text{T}_{\text{OH}}^-$  and collapse of  $\text{T}_0^-$  to form  $\text{CH}_2\text{NO}_2^-$ , show similar structure-reactivity behavior as the proton transfer, such as transition-state imbalances as manifested by  $\alpha_{\text{nuc}}^n > \beta_{\text{nuc}}^n$  for nucleophilic addition and depressed intrinsic rate constants. However, these imbalances are smaller compared to the one in the proton transfers, especially so for the nucleophilic addition to the olefin. It is suggested that there is an inherent tendency for reactions leading to resonance-stabilized ions to have imbalanced transition states, but in proton transfers there are two imbalance *enhancing* factors, namely  $\text{sp}^3$  hybridization of the carbon in the protonated form and hydrogen bonding in the transition state, while in the collapse of  $\text{T}_0^-$  there is one such factor ( $\text{sp}^3$  hybridization of the carbon in  $\text{T}_0^-$ ).

The mechanism of the hydrolysis of activated olefins,  $\text{ArCH}=\text{CXY}$  (X and Y are electron-withdrawing substituents), is shown in Scheme I.<sup>2</sup> During the past several years a number of detailed kinetic studies has been reported<sup>3</sup> which led to the determination of many of the rate constants that are shown in the scheme. Most steps in Scheme I refer to carbanion forming (or carbanion consuming) reactions:  $k_1$  leads to a carbanion by means of nucleophilic addition to the olefin,  $k_{-2}$  leads to the same carbanion by a proton transfer, and  $k_4$  generates a carbanion during the collapse of a tetrahedral intermediate. Hence, the determination of the rate and equilibrium constants of these

Scheme I



various steps as a function of X and Y can teach us a great deal about structure-reactivity patterns in carbanion-forming processes. With this aim in mind, we have undertaken an investigation of

(1) This is part 25 in the series Nucleophilic Addition to Olefins. Part 24: Bernasconi, C. F.; Killion, R. B. *J. Org. Chem.* 1989, 54, 2878.

(2) For reviews summarizing the earlier literature, see: (a) Patai, S.; Rappoport, Z. In *The Chemistry of the Alkenes*; Patai, S., Ed.; Wiley-Interscience: New York, 1964; Chapter 8. (b) Fyfe, C. A. In *The Chemistry of the Hydroxyl Group*; Patai, S., Ed.; Wiley-Interscience: New York, 1971; Chapter 2.

(3) (a) Bernasconi, C. F.; Leonarduzzi, G. D. *J. Am. Chem. Soc.* 1982, 104, 5133, 5143. (b) Bernasconi, C. F.; Carré, D. J.; Kanavarioti, A. *Ibid.* 1981, 103, 4850. (c) Bernasconi, C. F.; Howard, K. A.; Kanavarioti, A. *Ibid.* 1984, 106, 6827. (d) Bernasconi, C. F.; Laibelman, A.; Zitomer, J. L. *Ibid.* 1985, 107, 6563. (e) Bernasconi, C. F.; Kanavarioti, A.; Killion, R. B. *Ibid.* 1985, 107, 3612. (f) Bernasconi, C. F.; Fox, J. P.; Kanavarioti, A.; Panda, M. *Ibid.* 1986, 108, 2372. (g) Bernasconi, C. F.; Stronach, M. *J. Org. Chem.* 1986, 51, 2144.