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Silylative Decarbonylation. 2. Catalysis and Conversion to Heterogeneous Conditions[1]

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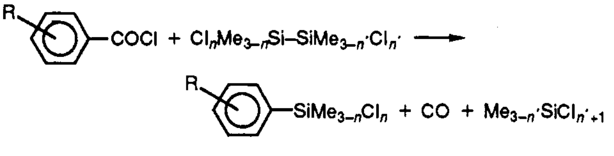
The silylative decarbonylation catalytic reaction between aromatic acid chlorides and chloromethyldisilanes (to yield arylchlorosilanes) was investigated with respect to ligand effects and attempts to convert the process to heterogeneous conditions. The rate of reaction was found to correlate directly to phosphine ligand donor ability. Amines are also effective cocatalysts, although less reactive than phosphines. The propensity for side reaction products, e.g., benzil or benzophenone, also increased with increasing ligand donor ability. Several commercially available heterogeneous catalysts were screened for the silylative decarbonylation process, and none was found that would mimic the results under homogeneous conditions. The reaction was successfully converted to heterogeneous conditions by employing a silica-bound "heterogeneous" catalyst. Activity and selectivity similar to solution phase results were found. The synthetic catalyst also showed promise for reaction of polychlorinated methyldisilanes that were less successful under homogeneous conditions.

Introduction

We have recently described a versatile synthetic approach to the preparation of aromatic chlorosilanes via the palladium-catalyzed reaction of aryl acid halides and chloromethyldisilanes[1a] (see eq 1). The silylative decarbonylation procedure is general with respect to substituents that can be placed on the aromatic acid halide, e.g., alkyl, alkoxy, cyano, halo, nitro, and carbonyl functionalities such as acid anhydride, acyl halide, or phthalimido groups, thus providing a one-step, high-yield (60–80%) route to functionalized aromatic chlorosilanes that were previously unavailable or were prepared via laborious multistep methods. The utility of a number of these aromatic silicone precursors has been described in the patent literature.[2]



(1)

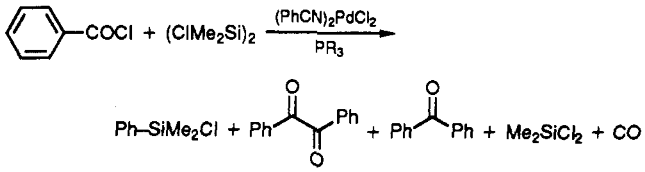
In determining the synthetic scope of the silylation reaction, a homogeneous catalyst system utilizing bis(benzonitrile)palladium dichloride and 2 mol equiv of triphenylphosphine was employed. Benzil derivatives, formed via a carbon–carbon coupling reaction, were found to be the major side products (10–15%) and benzophenone adducts were also identified in lesser amounts. In addition, introduction of phosphine causes an undesired disproportionation of polychlorinated disilanes such as *sym*-tetrachlorodimethyldisilanes.[3] These various side reactions lead to the formation of nonvolatile components that complicate the isolation of desired arylchlorosilanes, inevitably causing a decrease in the yield.

This report details parameters, particularly with regard to the catalyst, that control the ratio of products and various side reactions. Constraints of current economics with respect to precious metals also led us to investigate and optimize catalyst recovery and activity. The advantages of heterogeneous catalysts have been well documented, and so initial efforts were directed toward identifying available catalysts that would mimic the results observed in the previous homogeneous reactions.[4]

As described herein, several surprising results were found in the course of screening commercially available catalysts and none were found which were consistently similar to the homogeneous reactions. A successful solution was eventually found by taking a "homogeneous" system and anchoring it on a support material. This approach has often been described in the literature, but few examples exist where the "supported" catalyst functioned as well as the corresponding homogeneous compound.[4,5] The silylative decarbonylation reaction carried out with a "supported homogeneous" catalyst proceeds in a fashion almost identical with the dissolved catalyst itself and yet is readily recoverable and reusable.

Results and Discussion

I. Ligand Effect on Catalysis. A series of reactions designed to investigate the effect of changing the catalyst ligand on the product yields and reaction rates was carried out. In each example benzoyl chloride was reacted with 1,2-dichlorotetramethyldisilane utilizing 1 mol % bis(benzonitrile)palladium dichloride and 2 mol % added phosphine (1 mol % in the case of bidentate ligands such as DIPHOS). The experiments were carried out neat at 125 °C under an atmosphere of nitrogen and the product ratios determined by gas chromatography. A summary of the results is shown in Table I.



A control sample was run using the nitrile palladium complex without added phosphine (see entry 1, Table I). Under these conditions, addition of the catalyst to the reaction mixture resulted in immediate precipitation of palladium black metal that was not effective for carrying

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(1) (a) Part 1: Rich, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 5886. (b) Rich, J. D. U.S. Patent 4,709,054, 1987. (c) Rich, J. D. U.S. Patent 4,604,477, 1986. (d) Rich, J. D.; Krafft, T. E.; McDermott, P. J. U.S. Patent Application 232,242, 1988.

(2) U.S. Patent 4,604,442, 1986; U.S. Patent 4,678,610, 1987; U.S. Patent 4,668,754, 1987.

(3) (a) Calas, R.; Dunogues, J.; Delevis, G.; Duffaut, J. *J. Organomet. Chem.* **1982**, *225*, 117. (b) Baney, R.; Gaul, J.; Hilty, T. *Organometallics* **1983**, *2*, 859. (c) Matsumoto, H.; Okhawa, K.; Matsubara, I.; Kashara, M.; Arai, T.; Nagai, Y. *J. Organomet. Chem.* **1984**, *224*, 29.

(4) Hartley, F. R.; Vezey, P. N. *Adv. Organomet. Chem.* **1977**, *15*, 189.

(5) (a) Grubbs, R. H. *CHEMTECH* **1977**, *7*, 512. (b) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; p 370.

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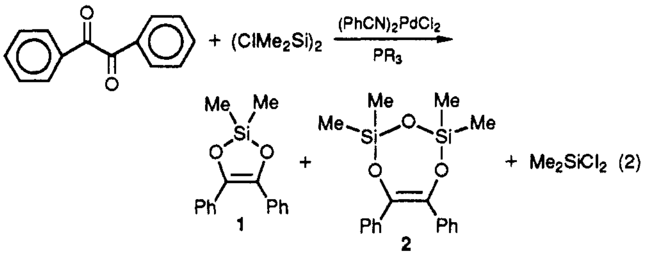
Table I. Effect of Catalyst/Cocatalyst on the Reaction of Benzoyl Chloride with 1,2-Dichlorotetramethyldisilane[a]

entry	cat.	% convn	% $PhMe_2SiCl$	% benzil	% benzophenone	% benzil derivative
1	$(PhCN)_2PdCl_2$/no PR_3			no reaction		
2	$(PhCN)_2PdCl_2/P(c\text{-}Hx)_3$	99	42	19	6	34
3	$(PhCN)_2PdCl_2/P(Bu)_3$	99	67	12	2	18
4	$(PhCN)_2PdCl_2/P(o\text{-}MeOPh)_3$	100	74	7	3	16
5	$(PhCN)_2PdCl_2/P(p\text{-}MePh)_3$	100	77	0	trace	23
6	$(PhCN)_2PdCl_2/P(Ph)_3$	87	67	15	2	3
7	$(PhCN)_2PdCl_2/P(p\text{-}ClPh)_3$			no reaction		
8	$(PhCN)_2PhCl_2$/DIPHOS			no reaction		
9	$(PhCN)_2PdCl_2/Et_3N$	54	38	8	trace	8
10	$(PhCN)_2PdCl_2$/Pyridine	79	61	8	trace	10
11	$(PhCN)_2PdCl_2$/TMEDA	53	36	14	trace	3
12	$Pd(PPh_3)_4$	95	72	12	2	9
13	$Pd(PPhMe_2)_2Cl_2$	98	60	20	7	10

[a] 1 mol % catalyst, neat, 125 °C, 15 h. [b] c-Hx = cyclohexyl.

out the silylative decarbonylation process. As a general rule, reactions carried out with bis(benzonitrile)palladium dichloride and added phosphine resulted in initial precipitation of palladium black followed by redissolution of the metal within the first half hour of reaction to give a homogeneous solution. It should be noted that while bis(benzonitrile)palladium dichloride alone did not affect the catalysis of benzoyl chloride, it was effective when used with much more reactive acid chlorides such as trimellitic anhydride acid chloride or *m*-nitrobenzoyl chloride. Even in these cases, the nitrile catalyst alone was not as reactive as the combination of bis(benzonitrile)palladium dichloride and added phosphine.

Catalysts of benzoyl chloride with 1,2-dichlorotetramethyldisilane using the nitrile complex and 2 equiv of added phosphine gave phenyldimethylchlorosilane as the major product in all cases where any reaction occurred. Benzil was the major side product in all examples tested with benzophenone formed in lesser amounts. Several other products were always observed whose GC retention times were longer than benzil. These compounds were identified as silylated derivatives of benzoin (see Eq 2).



Addition of tricyclohexylphosphine to a mixture of benzil and 1,2-dichlorotetramethyldisilane did not induce a reaction until bis(benzonitrile)palladium dichloride was also introduced. The combination of metal and phosphine cocatalysts caused rapid formation of the silylated benzoin derivatives in a ratio analogous to that seen in the decarbonylation reactions. The scope of this catalyzed reaction of disilanes with diketones is currently under investigation. The total yields of 1 and 2 in the reactions studied are listed for each example as "benzil derivatives" in Table I.

As shown in Table I, use of strong donor phosphine cocatalysts such as tricyclohexyl- or tri-*n*-butylphosphine (cyclohexyl = c-Hx) gave large amounts of benzil and silylated derivatives of benzil (entries 2 and 3). Triarylphosphine and tri-*o*-anisylphosphine and tri-*p*-tolylphosphine led to greater overall yields of benzil and benzil derivatives and were also more effective in converting benzil to its silylated products in comparison with triphenyl phosphine. Tris(*p*-chlorophenyl)phosphine was not an effective cocatalyst for the silylative decarbonylation reaction nor was the bidentate ligand DIPHOS. In the former case precipitation of palladium black occurred, while in the latter case a yellow complex was formed. The overall rate of reaction, as determined by monitoring CO gas evolution, appeared to directly correlate with the overall donor ability of the added phosphine. A relative ordering of reactivity is shown.

$$P(c\text{-}Hx)_3 \geq PBu_3 > P(o\text{-}CH_3OPh)_3,\ P(p\text{-}CH_3Ph)_3 > PPh_3 > \text{tertiary amines}$$

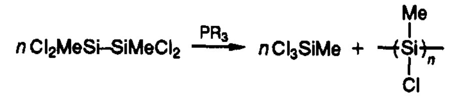
Tertiary amine derivatives were also effective as cocatalysts in the reaction of benzoyl chloride with 1,2-dichlorotetramethyldisilane although the rates of reaction decreased compared to the phosphine examples (see entries 9–11, Table I). Pyridine gave greater conversion and better yield of phenyldimethylchlorosilane than did triethylamine. Triethylamine gave a greater relative yield of benzil and benzil derivatives than pyridine. The bidentate nitrogen ligand tetramethylethylenediamine converted 53% of the starting acid chloride in the 15-h reaction time, yielding 36% phenyldimethylchlorosilane. By comparison, the bidentate phosphine adduct DIPHOS completely inhibited the silylative decarbonylation process.

Two preformed palladium phosphine adducts were also examined for their effectiveness as catalysts: tetrakis(triphenylphosphine)palladium(0), and bis(methyldiphenylphosphine)palladium(II) dibromide. Both were successful in carrying out the desired reaction; however, upon introduction of the palladium(0) complex, immediate precipitation of palladium black occurred which then redissolved and evolution of carbon monoxide ensued. In the case of the palladium(II) adduct, a continuously homogeneous reaction mixture was maintained although an induction period did occur before the initiation of gas evolution. As was previously seen, the stronger donor ligand complex bis(methyldiphenylphosphine)palladium dibromide gave greater amounts of benzil and was more effective in the subsequent silylation of benzil.

The experiments demonstrate a trade-off between optimizing the yield of desired arylchlorosilane, phenyldimethylchlorosilane in this case, and carrying out the reaction at the optimum rate. From a practical view, it is advantageous to minimize the amount of silylated derivatives of benzoin since these materials are highly nonvolatile, and the recovery of the desired arylchlorosilanes by distillation is hindered in the presence of these adducts. For this reason, the combination of bis(benzonitrile)palladium dichloride and triphenylphosphine was chosen for synthetic procedures as a compromise between rate and yield and also considering the ready availability of both the palladium and phosphine compounds.

II. Heterogeneous Catalyst Screening. We next turned our attention toward converting the homogeneous silylative decarbonylation process into a procedure that could utilize a supported heterogeneous catalyst. There were a number of important reasons for wanting to pursue this approach. Supported catalysts can be readily removed, reused, and potentially reactivated, making recovery of the metal easier than in homogeneous reactions. Metal recovery is often the determining factor in the economic viability of a catalytic industrial process. It was also hoped that judicious selection or design of a heterogeneous catalyst might minimize the yield of side products such as benzils, silylated benzoins, and benzophenones.

In the homogeneous process, introduction of the phosphine cocatalyst to polychlorinated disilanes such as *sym*-tetrachlorodimethyldisilane under standard homogeneous conditions results in a disproportionation process that competes with aromatic silylation for the disilane reagent (see eq 3). Minimization of this disproportionation process



$$n\,\mathrm{Cl_2MeSi{-}SiMeCl_2} \xrightarrow{\mathrm{PR_3}} n\,\mathrm{Cl_3SiMe} + \left(\underset{\mathrm{Cl}}{\overset{\mathrm{Me}}{\mathrm{Si}}}\right)_n \qquad (3)$$

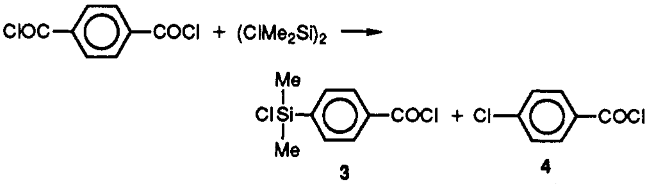
is important because reaction of substituted acid chlorides with *sym*-tetrachlorodimethyldisilanes yields arylmethyldichlorosilanes which, upon hydrolysis, incorporate the arylsiloxane into the backbone of the resultant polymer. *sym*-Tetrachlorodimethyldisilane is also the major constituent of the methylchlorosilane direct process residues, making this compound an attractive precursor to aryl-substituted silicones. We hoped that a heterogeneous catalyst system could be developed that would minimize the disproportionation reaction and still catalyze the reaction of polychlorinated disilanes with aromatic acid chlorides.

Our initial approach was to screen a variety of commercially available supported palladium catalysts for their effectiveness in the silylative decarbonylation reaction. Some of the criteria for evaluating the heterogeneous catalysts were (1) to maintain the generality of the reaction with respect to aryl and silicon substituents as was observed under homogeneous conditions,[1] (2) to equal or surpass the ratio of desired aromatic chlorosilanes to various unwanted side products, (3) to be useful as a silylation catalyst in reactions of polychlorinated disilanes with aromatic acid chlorides while not being a catalyst for the disproportionation of the disilane to polysilane, and (4) to be readily removable, recoverable, and reusable.

Several commercially available heterogeneous catalysts (e.g., Pd/C, Pd/alumina, Pd/silica, see Table II) were screened to determine their effectiveness in the silylative decarbonylation process. The first silylation of terephthaloyl chloride with 1,2-dichlorotetramethyldisilane was used for the study because the reaction occurred at a relatively fast rate and was convenient for GC analysis.[1] The results are shown in Table II. Each reaction was carried out at 145 °C neat for 15 h by using 0.5 mol % total palladium. Extreme variances were seen in the course of the reactions depending upon the loading, source, and nature of the support material. Unlike the homogeneous reactions investigated, the major side reaction with the supported catalysts that were screened was decarbonylation without incorporation of the silicon or, in this case, formation of *p*-chlorobenzoyl chloride.

Entry 1 (Table II) shows the control experiment of terephthaloyl chloride with 1,2-dichlorotetramethyldisilane using standard homogeneous conditions of bis(benzonitrile)palladium chloride and triphenylphosphine. Complete conversion of the starting acid chloride occurs after 15 h giving a greater than 20:1 ratio of *p*-(chlorodimethylsilyl)benzoyl chloride to *p*-chlorobenzoyl chloride. Palladium black (entry 2), formed by the introduction of palladium dichloride, gave only 10% conversion after 15 h, but the ratio of **3** to **4** was 10:1.

Table II. Supported Catalyst Activity/Selectivity: 1,2-Dichlorotetramethyldisilane and Terphthaloyl Chloride[a]



entry	cat.	% convn	ratio 3:4
1	homogeneous $(PhCN)_2PdCl_2$	100	>20:1
2	Pd metal from $PdCl_2$	10	10:1
3	10% Pd/C 325 mesh (MCB)	100	3:5
4	10% Pd/C 325 mesh (Aldrich)	100	9:10
5	1% Pd/C 12–30 mesh (Johnson Mathey (JM))	89	21:1
6	2–5% Pd/C 4–8 mesh (JM)	59	14:1
7	10% Pd/silica powder (Engelhardt (Eng))	8	1:8
8	5% Pd/C 4–8 mesh, steam activated wood carbon (JM)	not effective in reaction	
9	0.5% Pd/alumina high surface extrudate (Eng)	not effective in reaction	

[a] 0.5% Pd, 15 h, 145 °C, neat.

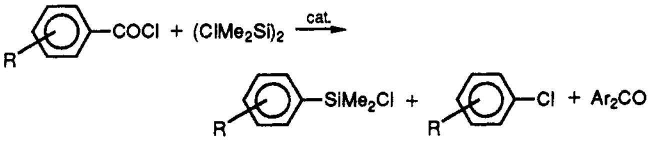
Two samples of 10% Pd on charcoal from different sources (MCB and Aldrich) were utilized, and both showed good reactivity with complete consumption of the starting material after 15 h. However, both showed a preference for decarbonylation without incorporation of the silicon. In entry 3, a 3:5 ratio of *p*-(chlorodimethylsilyl)benzoyl chloride to *p*-chlorobenzoyl chloride was observed, while in example 4 the ratio was 9:10.

A sample of Johnson-Mathey catalyst 1% Pd on carbon (12–30 mesh) was examined and showed good activity, 89% conversion, and showed excellent selectivity with a 21:1 ratio of **3** to **4** found. Another Johnson-Mathey catalyst, 2–5% Pd on 4–8 mesh carbon, was slightly less active but still gave a good ratio, 14:1 of **3** to **4** (see entry 6). A catalyst comprising 10% Pd on silica (Engelhardt) (entry 7) not only demonstrated poor reactivity with only 8% conversion after 15 h but only yielded a 1:8 ratio of products **3**:**4**.

Introduction of 0.5% palladium on high surface alumina to a standard reaction mixture resulted in a very fast reaction, as determined by carbon monoxide outgassing in comparison to other heterogeneous catalysts examined. Analysis of the product mixture by GC showed that a completely different type of reaction had taken place. Complete consumption of the starting acid chloride occurred, but neither *p*-(chlorodimethylsilyl)benzoyl chloride nor *p*-chlorobenzoyl chloride was formed. When the same catalyst was utilized in the reaction of benzoyl chloride with 1,2-dichlorotetramethyldisilane, benzophenone was the major product formed alone with several as yet unidentified compounds. This type of reactivity was not limited to alumina-supported catalysts. A sample of 5% Pd on steam activated wood carbon, obtained from Johnson-Mathey through Aesar, behaved almost analogously to the sample of palladium on alumina.

We are currently trying to rationalize this behavior, but the results of our initial screening did not allow us to make any predictions concerning the selection or reproducibility of the available catalysts. In all cases it was found that

Table III. Selectivity of Johnson-Mathey 1% Pd/C 12-30 Mesh[a]



substrate	% Ar-Si	% Ar-Cl	% Ar_2CO
PhCOCl	trace	78	10
m-$CH_3PhCOCl$	7	52	24
p-ClOCPhCOCl	76	24	0
m-$NO_2PhCOCl$	67	7	7
3,4-anhydride PhCOCl	90	10	0

[a] 1% catalyst, 145 °C, neat, 15 h (>98% conversion).

addition of phosphines to reaction mixtures containing supported catalysts did not have any adventitious effects and in fact acted as catalyst poisons in most cases.

The catalyst shown in Table II, entry 5, appeared to have reactivity and selectivity most similar to the homogeneous examples and so further testing was undertaken. A series of experiments were carried out by using Johnson-Mathey 1% Pd on 12-30 mesh carbon (similar to that in Table II, entry 5, but from a different lot number) to catalyze the reaction between substituted aryl acid chlorides and 1,2-dichlorotetramethyldisilane. Each reaction was carried out neat at 145 °C for 15 h (>98% conversion was observed in all cases). Unlike the homogeneous reactions, the 1% Pd on 12-30 mesh carbon catalyst gave product ratios that were directly related to the electron-withdrawing ability of the substituent on the aromatic acid chloride. The results are shown in Table III.

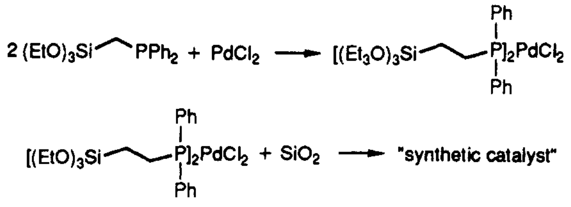
Catalysis of trimellitic anhydride acid chloride with 1,2-dichlorotetramethyldisilane gave a 90:10% relative yield of 4-(chlorodimethylsilyl)phthalic anhydride to 4-chlorophthalic anhydride. Reaction of the same disilane with benzoyl chloride under analogous conditions gave none of the silylated compound phenyldimethylchlorosilane but instead yielded 78% chlorobenzene and 10% benzophenone. There was no evidence for benzil formation. When a stronger donor acid chloride was employed, m-toloyl chloride, the amount of benzophenone-type product increased relative to chlorotoluene (see entry 2). Increasing electron-withdrawing ability on the reactant acid chloride resulted in an increased relative yield of the desired silylated aromatic derivative. In the case of terephthaloyl chloride, the ratio of 4-(chlorodimethylsilyl)benzoyl chloride to 4-chlorobenzoyl chloride was only 3:1 compared to 21:1 with the same catalyst but from a different lot number.

It is well-known that the palladium catalyzed decarbonylation of aromatic acid chlorides to give the corresponding chloro aromatic compounds occurs only at temperatures greater than 250 °C.[6] Considering this, it is difficult to rationalize the formation of chlorobenzene in the reactions described in Table III without incorporating the disilane material as playing some part in the catalysis. To test this, benzoyl chloride was placed in the presence of the 1% Pd on 12-30 mesh catalyst at 145 °C. After 3 days under these conditions, absolutely no reaction had occurred and no evidence for the formation of chlorobenzene could be found. A sample of the same catalyst was then placed in an excess of 1,2-dichlorotetramethyldisilane for 1 h at room temperature followed by filtration and washing with toluene and hexane. After the material was dried under nitrogen, the treated catalyst was introduced to benzoyl chloride and the mixture heated to 145 °C. After 15 h, 45% of the starting acid chloride had been converted to chlorobenzene. Clearly the disilane acts in some fashion, perhaps as a reducing agent or a ligating material, to activate the supported catalyst toward the decarbonylation reaction.

The results of our initial screening of potential heterogeneous catalysts demonstrate the difficulty in selecting a reproducible material. Extreme variances were found even within the same class of support material, e.g., carbon-based catalysts. Although certain catalysts were found (e.g., Table II, entry 5) which behaved similarly to the homogeneous reactions with certain strong electron-withdrawing substituted aryl acid chlorides, reaction with other substrates such as benzoyl chloride itself gave completely different results. These examples would seem typical of the aggravations often confronted in developing heterogeneous systems.

III. Preparation and Reactivity of the Synthetic Catalyst. The variability of those commercially available catalysts that were examined as well as the dependence of product ratios on the nature of the aromatic substituent prompted us to investigate the possibility of "tailoring" a homogeneous catalyst that could be anchored later onto a heterogeneous support material. This approach has been widely documented for other catalytic reactions, and anchoring on inorganic as well as polymeric organic substrates has been described.[4,5] Our initial studies focused on a previously described palladium(II) catalyst supported on silica.[7]

Bis[((diphenylphosphino)ethyl)triethoxysilyl]palladium dichloride was prepared by known procedures and was anchored on silica by hydrolysis of the triethoxysilyl groups to give a supported catalyst with 1 wt % loading of palladium metal. This catalyst was examined for its activity and selectivity in the silylative decarbonylation reactions of aromatic acid chlorides and disilanes. In each case the aromatic acid chloride was reacted neat with 1,2-dichlorotetramethyldisilane at 145 °C for 15 h in the presence of 1 mol % palladium in the form of the supported synthetic catalyst. The results are shown in Table IV.



The reactivity and activity of the synthetic catalyst were found to be almost identical with reactions carried out under homogeneous reaction conditions. When benzoyl chloride was employed, a 70% yield of phenyldimethylchlorosilane was observed, as well as 22% benzil formation. Only 3% chlorobenzene and 4% benzophenone were found in the product mixture. Use of p-toluoyl chloride gave results similar to benzoyl chloride. Catalysis of aromatic acid chlorides containing stronger electron-withdrawing substituents led to better yields of the desired silylated aromatics.

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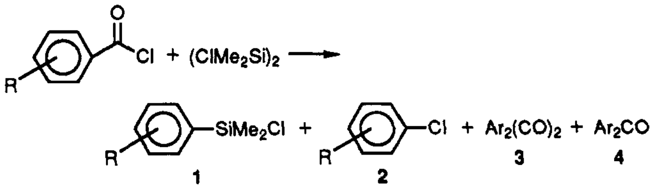
(6) (a) Tsuji, J. In *Organic Synthesis via Metal Carbonyls*; Pino, P., Wender, I., Eds.; Wiley-Interscience: New York, 1977; Vol. II, p 633. (b) Verbicky, J. W.; Dellacolleta, B.; Williams, L. *Tetrahedron Lett.* **1982**, 371.

(7) (a) Allum, K. G.; Hancock, R. D.; Howell, I. V.; McKenzie, S.; Pitkethly, R. C.; Robinson, P. J. *J. Organomet. Chem.* **1987**, *87*, 203. (b) Allum, K. G.; Hancock, R. D.; Howell, I. V.; Lester, T. E.; McKenzie, S.; Pitkethly, R. C.; Robinson, P. J. *J. Catal.* **1976**, *43*, 331. (c) Allum, K. G.; McKenzie, S.; Pitkethly, R. C. U.S. Patent 3,726,809, 1973.

Table IV. Selectivity of the Synthetic Catalyst[a]



substrate, R	% 1	% 2	% 3	% 4
H	70	3	22	4
p-Me	74	3	21	2
p-Cl	91	trace	9	trace
p-COCl	90	trace	10	trace
3,4-anhydride	98		1	

[a] 1% catalyst, 145 °C, 15 h, neat.

The silica-supported catalyst could be readily recovered by filtration. After the solution was washed with methylene chloride and dried under nitrogen, reintroduction to fresh reagents resulted in carbon monoxide evolution and formation of the arylchlorosilane product. Some loss in activity was noted however. Figure 1 shows preliminary results of a catalyst lifetime study of the silica-supported synthetic catalyst in comparison with the 1% Pd on 12–30 mesh carbon catalyst which was found to be the most effective available catalyst tested. Equimolar amounts of terephthaloyl chloride and 1,2-dichlorotetramethyldisilane were heated neat to 145 °C, and 3 mol % palladium catalyst was introduced. (Each catalyst had a loading level of 1 wt % and stoichiometries were calculated on the basis of palladium metal.) Each experiment was carried out for 3 h after which the catalyst was removed by filtration and the product mixture determined by GC (relative to dodecane internal standard). After the catalyst was washed and dried, it was introduced to fresh aliquots of disilane and terephthaloyl chloride and the experiment repeated.

As shown in Figure 1, both types of catalysts showed decreases in activity from the first to second and subsequently third runs, although the activity of the silica-supported synthetic catalyst was greater than the carbon material. After three cycles the silica catalyst showed 60% of its initial activity while the carbon material had only 35% activity. Fresh silica catalyst was bright yellow in appearance while the material recovered after the third run was dull orange-brown. The used catalyst was slurried in carbon tetrachloride, and chlorine gas was introduced causing a conversion of the catalyst back to a bright yellow similar to freshly prepared material. Reintroduction of the chlorine treated catalyst to fresh aliquots of terephthaloyl chloride and tetramethyldichlorodisilane resulted in increasing the activity of the reaction back to 80% of the initial catalytic conversion. After recovery, the activity again decreased to 60% initial conversion in the fifth run. Treatment of the carbon based palladium with chlorine did not cause any recovery of activity, and after the fifth run the material was no longer effective in converting acid chloride to arylsilane.

The silica-bound palladium catalyst was also investigated with respect to utility in the reaction of *sym*-tetrachlorodimethyldisilane and substituted aryl acid chlorides. It was our hope that binding of the silylated phosphine to the support might effectively shield the disilane from nucleophilic attack by the ligand. Indeed it was observed that the silica-bound catalyst was more effective than the homogeneous catalysts in the synthesis of arylmethyldichlorosilanes.

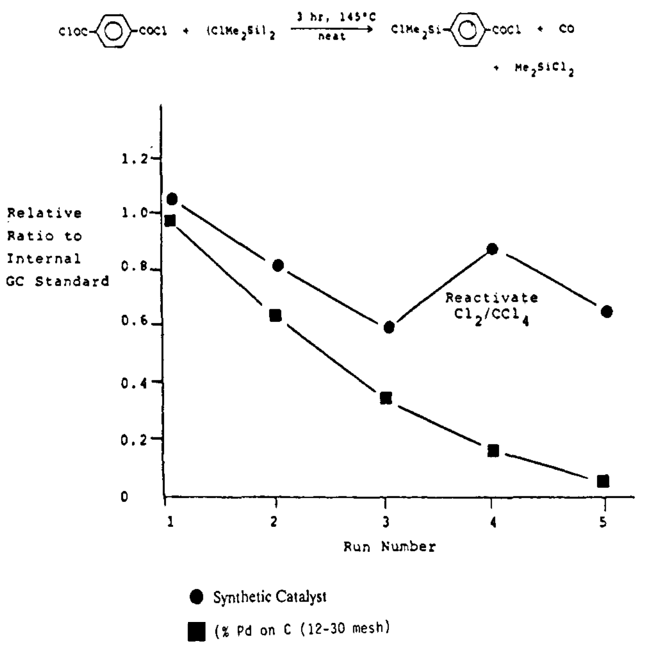
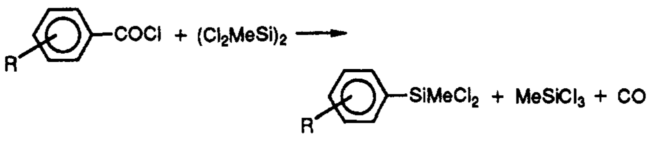
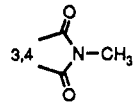
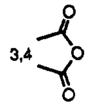


Figure 1. Synthetic catalyst performance.

Table V. Synthesis of Arylmethyldichlorosilanes via the Synthetic Catalyst[a]



substrate, TC	% ArSiMeCl$_2$	% ArCl
H	90	10
p-Cl	89	11
	36	7
	95	5

[a] 1% catalyst, 130–135 °C, neat, 15 h.

A summary of the reactions of *sym*-tetramethyldichlorodisilane with substituted aryl acid chlorides is shown in Table V. Careful control of the reaction parameters was necessary to optimize the yield of desired arylmethyldichlorosilane. Temperature control was particularly critical and running at the minimum amount necessary to maintain a reasonable reaction rate was optimum. As was previously observed with homogeneous reactions, catalysis with acid chlorides containing electron-withdrawing substituents gave greater yields and had faster reaction rates than donor or neutral acid chlorides. Comparison of the conversion rates points out this fact. After 15 h at 130–135 °C only 18% of benzoyl chloride was converted to product compared to 93% in the case of trimellitic anhydride acid chloride.

The selectivity of the reaction, as determined by the ratio of silylated aromatic product to arylchloride when *sym*-tetrachlorodimethyldisilane was utilized, was similar to the results seen for 1,2-dichlorotetramethyldisilane (see Table V). Reaction with benzoyl chloride gave a 9:1 ratio of phenylmethyldichlorosilane to chlorobenzene. Similar ratios were observed for reactions involving *p*-chlorobenzoyl chloride, terephthaloyl chloride, and trimellitic anhydride acid chloride. The yield and ratio of products of catalysts with *N*-methyltrimellitimide acid chloride were significantly less.

Failure of the desired silylative decarbonylation process and subsequent disproportionation of the reactant polychloromethyldisilane could be qualitatively noted by a change in the catalyst appearance from the usual orange color to a very bright red. This change was accompanied by rapid distillation of chlorinated methylsilane, methyltrichlorosilane in the case of *sym*-tetrachlorodimethyldisilane, and ceasing of carbon monoxide evolution. Preliminary investigations into the degradation mechanisms of the supported silica catalyst have shown that a net loss of palladium and phosphine occurs during each run. The magnitude of this loss is a function of reaction temperature and ligand substrate structure. These results suggest that phosphine is slowly being leached into the reaction mixture and may be the cause of the undesired disproportionation processes which occur as the extent of reaction increases. Details of these studies will be released in a future paper.

Conclusions

This study has investigated the effect of ligands on the homogeneous reaction of methylchlorodisilanes and aromatic acid chlorides and has documented our initial efforts in converting the process into one which can utilize a recoverable heterogeneous catalyst. Both phosphine and amine cocatalysts were effective in the silylative decarbonylation reaction, with the former giving greater reaction rates. In general, the observed reaction rate was directly related to the donor ability of the phosphine ligand. The donor ability of the phosphine also could be correlated to the amount and nature of the side products that were formed. For laboratory scale reactions done under homogeneous conditions, the combination of bis(benzonitrile)palladium dichloride and triphenylphosphine is recommended.

Attempts to find a commercially available heterogeneous catalyst that would perform analogously to the homogeneous system were unsuccessful, although our search did not include an exhaustive examination of every available catalyst. Variances were noted on the nature of the reaction pathway depending on the source of the catalyst, and there appear to be no systematic trends that allow predictions as to the success or failure of any particular example.

A silica-bound "homogeneous" catalyst was found to have activity and selectivity that were nearly identical with the solution reactions. This catalyst was readily removable and reusable and showed promise in reactions with polychloromethyldisilanes which were unsuccessful in homogeneous reactions. Some leaching of the active metal from the support was noted, and the extent of this problem is currently under investigation.

Experimental Section

General Data. All reactions were carried out under nitrogen unless noted, although no precautions were taken to rigorously exclude air or moisture. All acid chlorides were commercially available and were used as received (purity >97%). 1,2-Dichlorotetramethyldisilane was distilled from methylchlorosilane direct process residues or could be prepared by previously described methods.[8] Commercial catalysts were obtained from MCB, Aldrich, Johnson-Mathey Corp., and Engelhardt and were used as received. After opening, the materials were stored so as to avoid moisture absorption. Silica was obtained from MCB and PQ Corps. (Diphenylphosphino)ethyltriethoxysilane was prepared as previously described.[7a]

Effect of Phosphine Ligand Cocatalyst on the Bis(benzonitrile)palladium Dichloride Reaction of Substituted Aromatic Acid Chlorides with 1,2-Dichlorotetramethyldisilane. Each reaction was carried out under analogous conditions utilizing 1 mol % bis(benzonitrile)palladium dichloride and 2 mol % added phosphine or amine (1 mol % in the case of bidentate ligands such as DIPHOS or TMEDA); for example, the case of triphenylphosphine is exemplified.

GC response factors for authentic samples of chlorobenzene, benzoyl chloride, phenyldimethylchlorosilane, benzophenone, benzil, and 1,2-dichlorotetramethyldisilane were detd. on a Shimadzu GC9A instrument utilizing 8 ft × $^1/_8$ in. 10% SE30 on Chromosorb W 100/120 column with TCD detection. A reaction mixture containing 2.5 g (1.78×10^{-2} mol) of benzoyl chloride, 3.83 g (2.04×10^{-2} mol) of 1,2-dichlorotetramethyldisilane, 79 mg (2.03×10^{-4} mol) of bis(benzonitrile)palladium dichloride, and 108 mg (4.1×10^{-4} mol) of triphenylphosphine were heated neat at 125 °C under an atmosphere of nitrogen. After 15 h reaction time, an aliquot was removed and analyzed by GC. Analysis showed 83% conversion of benzoyl chloride to give (relative yields) 82% phenyldimethylchlorosilane, 10% benzil, 7% chlorobenzene, and 1% benzophenone.

Reactions using homogeneous preformed catalyst were run under identical conditions, except that 735 mg (2.04×10^{-4} mol) of tetrakis(triphenylphosphine)palladium was used in example 12 and 136 mg (2.04×10^{-4} mol) of bis(methyldiphenylphosphine)palladium dibromide was used in example 13.

Heterogeneous Catalyst Screening Experiments. Bis(benzonitrile)palladium dichloride was prepared as previously described.[9] $PdCl_2$ (entry 2, Table II), 1% Pd/C 12–30 mesh (entry 5), and 2–5% Pd/C 4–8 mesh (entry 6) were obtained direct from Johnson-Mathey Corp. Pd/SiO_2 powder (10%) (entry 7) and 0.5% Pd/high surface alumina extrudates (entry 9) were obtained from Engelhardt Minerals. The 5% Pd/C 4–8 mesh steam activated wood carbon (entry 8) was obtained from Johnson-Mathey through Aesar. Two samples of 10% Pd/C powder were obtained (entries 3 and 4) from MCB and Aldrich Chemical Co.

Response factors for terephthaloyl chloride, *p*-chlorobenzoyl chloride, and *p*-chlorodimethylsilylbenzoyl chloride were obtained on a Shimadzu GC9A utilizing an 8 ft × $^1/_8$ in. 10% SE 30 on Chromosorb W 100/120 column. In a typical experiment, 1.5 g (7.4×10^{-3} mol) of terephthaloyl chloride and 3.0 g (1.6×10^{-2} mol) of 1,2-dichlorotetramethyldisilane were heated neat at 145 °C in the presence of 0.5 mol % palladium (metal). After 15 h an aliquot was removed and analyzed by GC. Results are tabulated in Table II.

Reaction of Benzil with 1,2-Dichlorotetramethyldisilane in the Presence of Tri-*p*-tolylphosphine and Bis(benzonitrile)palladium Dichloride. A reaction mixture containing 2.0 g (9.53×10^{-3} mol) of benzil, 1.78 g (9.53×10^{-3} mol) of 1,2-dichlorotetramethyldisilane, and 144 mg (4.74×10^{-4} mol) of tri-*p*-tolylphosphine was mixed together neat at 145 °C under nitrogen. After 5 h no reaction had occurred and the starting materials remained intact. At that point, 100 mg (2.5×10^{-4} mol) of bis(benzonitrile)palladium dichloride was introduced, initiating a rapid reaction from which dimethyldichlorosilane was distilled. After 2 h at 145 °C, a 72% yield of the dimethylsilyl cyclic enol ether 1 of benzoin was obtained. GCMS analysis confirmed the formation of the tetramethyldisiloxane enol ether 2 as well.

Effect of Aromatic Substituents on the Catalysis of Aryl Acid Chlorides and 1,2-Dichlorotetramethyldisilane by Johnson-Mathey 1% Pd/C 12–30 Mesh. Each reaction was carried out utilizing 20 mmol of acid chloride, 20 mmol of 1,2-dichlorotetramethyldisilane, and 1 mol % of palladium (metal) as 1% Pd/C 12–30 mesh (Johnson-Mathey). The mixtures were heated neat at 145 °C for 15 h under a nitrogen atmosphere and were then analyzed by GC. The results are shown in Table III.

Registry No. DIPHOS, 1663-45-2; TMEDA, 110-18-9; PhCOCl, 98-88-4; *m*-$CH_3PhCOCl$, 1711-06-4; *p*-ClOCPhCOCl,

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[8] (a) Kumada, M.; Yamaguchi, M.; Yamamoto, Y.; Nakajima, J.; Shiina, K. *J. Org. Chem.* **1956**, *21*, 1264. (b) Reedy, D.; Urry, G. *Inorg. Chem.* **1967**, *6*, 2117. (c) Barton, T.; Banashiak, D. *J. Organomet. Chem.* **1975**, *157*, 255.

[9] Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

100-20-9; m-$\mathrm{NO_2PhCOCl}$, 121-90-4; p-$\mathrm{ClPhCOCl}$, 122-01-0; $\mathrm{(ClMe_2Si)_2}$, 4342-61-4; $\mathrm{(Cl_2MeSi)_2}$, 4518-98-3; $\mathrm{PhMe_2SiCl}$, 768-33-2; p-$\mathrm{ClOCPhSiMe_2Cl}$, 17902-45-3; m-$\mathrm{NO_2PhSiMe_2Cl}$, 116088-85-8; p-$\mathrm{CH_3PhSiMe_2Cl}$, 17881-63-9; p-$\mathrm{ClPhSiMe_2Cl}$, 825-92-3; $\mathrm{PhSiMeCl_2}$, 149-74-6; p-$\mathrm{ClPhSiMeCl_2}$, 825-93-4; $\mathrm{(PhCN)_2PdCl_2}$, 14220-64-5; P(c-Hx)$_3$, 2622-14-2; P(Bu)$_3$, 998-40-3; P(o-MeOPh)$_3$, 4731-65-1; P(p-MePh)$_3$, 1038-95-5; $\mathrm{PPh_3}$, 603-35-0; P(p-ClPh)$_3$, 1159-54-2; $\mathrm{Et_3N}$, 121-44-8; $\mathrm{Pd(PPh_3)_4}$, 14221-01-3; $\mathrm{Pd(PPhMe_2)_2Cl_2}$, 15616-85-0; Pd, 7440-05-3; trimellitic acid anhydride chloride, 1204-28-0; N-methyltrimellitimide acid chloride, 3969-16-2; 4-(chlorodimethylsilyl)phthalic anhydride, 116088-82-5; 4-(dichloromethylsilyl)-N-methylphthalimide, 115609-78-4; 4-(dichloromethylsilyl)phthalic anhydride, 104209-26-9; pyridine, 110-86-1.

Dimethylzirconocene-Catalyzed Polymerization of Alkylsilanes

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The polymerization of n-butylsilane was carried out using bis(η^5-cyclopentadienyl)dimethylzirconium(IV) as the catalyst. Rapid conversion of the silane to low molecular weight catenated Si–Si oligomers took place. The characterization revealed that a large percentage of the $\mathrm{Si_5}$ through $\mathrm{Si_7}$ oligomers were cyclic, whereas previous reports cited only linear products from similar reactions. Oligomers with degrees of polymerization (Dp) of 2 through 8 were also observed showing clear demonstration of a step growth mechanism. The difference in products is believed to be due to the ability of zirconium to react reversibly with both primary and secondary alkylsilanes. The lability of the zirconium–silicon bond allows for a dynamic equilibrium in which intermediate products are liberated from the metal center. These intermediates undergo further reaction including cyclization. Some possible mechanistic implications are discussed in light of previous literature postulates.

Introduction

Polysilanes have received a large amount of attention in the literature due to their potential uses as positive and negative photoresist materials, as photopolymerization catalysts, and as precursors to and reinforcing agents in ceramic materials.[1-3] The only viable route to high molecular weight polysilanes to date has been through the Wurtz coupling reaction, which has several commercial drawbacks: (1) poor control over molecular weight and large polydispersity, (2) potential hazards associated with the use of molten alkali metals, and (3) large amounts of salt waste generated.

Recently, the possibility of using transition metals to catalyze Si–Si catenation has been addressed by using group VII and group VIII transition-metal complexes,[4] but the best results for preparing longer Si–Si chains catalytically has been with group IV complexes. Harrod and co-workers have been the primary investigators of the group IV catalysts using bis(η^5-cyclopentadienyl)dimethyltitanium(IV) ($\mathrm{Cp_2TiMe_2}$) and bis(η^5-cyclopentadienyl)dimethylzirconium(IV) ($\mathrm{Cp_2ZrMe_2}$) in the dehydrogenative coupling of primary organosilanes.[5a-f] Their method employs alkyl or aryl silanes as monomers in the catenation reaction (eq 1).

$$n\mathrm{RSiH_3} \xrightarrow{\mathrm{Cp_2TiMe_2}} \mathrm{H{-}(R{-}SiH)}_n\mathrm{{-}H} + (n-1)\mathrm{H_2} \qquad (1)$$

Harrod and co-workers focused primarily on the use of phenylsilane ($\mathrm{PhSiH_3}$) as the substrate and $\mathrm{Cp_2TiMe_2}$ as the catalyst in these reactions. Although they report results from $\mathrm{Cp_2ZrMe_2}$ catalysis and other aryl- and alkylsilanes as substrates, most of the conclusions are drawn from the $\mathrm{PhSiH_3}$ work and extrapolated to include the other silane substrates and the zirconium catalyst.

Harrod's polysilane products were characterized by a number of spectral and chromatographic techniques and were claimed to be linear with Dp values between 10 and 20, but all analyses were carried out on bulk product mixtures. There is no evidence that individual components have been characterized. Harrod further claims that no low Dp species (Dp = 2–6) were detectable.

Our results using $\mathrm{PhSiH_3}$ are in reasonable agreement with those reported by Harrod et al., but, in our hands, alkylsilanes give a very different chemistry with $\mathrm{Cp_2ZrMe_2}$. Herein, we focus on the chemistry of n-butylsilane ($\mathrm{BuSiH_3}$) as the substrate for the $\mathrm{Cp_2ZrMe_2}$-catalyzed dehydrogenative coupling reaction. We chose this substrate for its small size, giving more facile analysis by gas chromatographic techniques. This zirconium-catalyzed process gives both linear and cyclic products with Dp values

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(1) (a) Zeigler, J. M.; Harrah, L. A.; Johnson, A. W. *Polym. Prepr.* **1987**, *28*(1), 424. (b) Harrah, L. A.; Zeigler, J. M., *Macromolecules* **1987**, *20*, 2039.

(2) (a) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. (b) Gilman, H.; Atwell, W. H.; Schwebke, G. L. *J. Organomet. Chem.* **1964**, *2*, 369. (c) Baney, R. H.; Gaul, J. H.; Hilty, T. K. (*Organometallics* **1983**, *2*, 859. (d) Gobbi, G. C.; Fleming, W. W.; Sooriyakumaran, R.; Miller, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 5624. (e) Yajima, S.; Shishodo, T.; Kayano, H. *Nature (London)* **1976**, *264*, 237. (f) Wolff, A. R.; West, R.; Peterson, D. G. Eighteenth Organosilicon Symposium, April, 1984. (g) Yajima, S. *Am. Ceram. Soc. Bull.* **1983**, *62*, 893.

(3) (a) Zeldin, M., Allcock, H. R., Wynne, K., Eds. *Inorganic and Organometallic Polymers*; ACS Symposium Monograph 360; American Chemical Society: Washington, DC, 1988. (b) Ed. Laine, R. M. *Transformation of Organometallics into Common and Exotic Materials: Design and Activation*; NATO AST Series E, 1988; No. 141.

(4) (a) Pannell, K. H.; Vincenti, S. P.; Scott, R. C., III *Organometallics* **1987**, *6*, 1593. (b) Corey, J. Y.; Chang, L. S.; Corey, E. R. *Organometallics* **1987**, *6*, 1595. (c) Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590.

(5) (a) Aitken, C.; Harrod, J. F.; Samuel, E. *J. Organomet. Chem.* **1985**, *279*, C11–C13. (b) Aitken, C. T.; Harrod, J. F.: Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059. (c) Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, *6*, 1381. (d) Harrod, J. F. *Polym. Prepr.* **1987**, *28*(1) 403. (e) Aitken, C.; Harrod, J. F.; Samuel, E. *Can, J. Chem.* **1986**, *64*, 1677. (f) Aitken, C.; Harrod, J. F.; Gill; U. S. *Can. J. Chem.* **1987**, *65*, 1804.

0276-7333/89/2308-2615$01.50/0