skeletal mode of $(CH_3)_2Te$ (526 cm^{-1}). This excellent correlation allows the assignment of this peak in the spectrum of ion **1** to the symmetric stretching vibration ν_6 for the C–I$^+$–C skeleton.

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A New Method of Forming the Carbon–Silicon Bond. Reductive Silylation of Aromatic Acids

Sir:

It is well recognized that only a limited number of chemical reagents are available which can bring about the reduction of a carboxyl group.[1] Previously[2, 3] we described the potency of certain trichlorosilane–tertiary amine combinations as reducing agents. We now wish to report a novel reaction in which the latter effects the reduction of benzoic acid and certain of its derivatives to benzylic trichlorosilanes in good yields.

Table I. Reductive Silylation of Aromatic Acids by Trichlorosilane–Tri-*n*-propylamine

Run	Reactants[a]	Conditions[b]	Products[c,d]	
1	$C_6H_5CO_2H$	14 hr, 77–82°	$C_6H_5CH_2SiCl_3$	(58%)
2	*p*-$ClC_6H_4CO_2H$	16 hr, 73–77°	*p*-$ClC_6H_4CH_2SiCl_3$[e]	(69%)
3	*p*-$BrC_6H_4CO_2H$	15 hr, 72–79°	*p*-$BrC_6H_4CH_2SiCl_3$	(58%)
4	*p*-$CH_3C_6H_4CO_2H$	16 hr, 71–77°	*p*-$CH_3C_6H_4CH_2SiCl_3$	(56%)
5	3,5-$(CH_3)_2C_6H_3CO_2H$	18 hr, 75–82°	3,5-$(CH_3)_2C_6H_3CH_2SiCl_3$	(51%)

[a] In every case, the mole ratio of acid:$SiHCl_3$:$(n\text{-}C_3H_7)_3N$ was 1:5:2. [b] In all cases, about 100 ml of acetonitrile was used as solvent. [c] In every instance, the percentage given in parentheses represents the *isolated* yield of organosilane based upon the weight of the starting acid. In addition, isolated yields of tri-*n*-propylamine hydrochloride ranging from 86 to 98% were obtained. [d] In the case of the silanes resulting from runs 1, 2, and 4, identification was made by matching their spectra (ir and nmr) with authentic samples. Satisfactory elemental analyses and spectral data (ir and nmr) were obtained for the silanes resulting from runs 3 and 5. [e] It is likely that tri-*n*-butylamine can be substituted for the tri-*n*-propylamine in every case. A 65% yield of *p*-chlorobenzyltrichlorosilane was realized when such a substitution was made in this run.

The overall process, which can again be termed a "reductive silylation,"[3] can be represented as follows

$$RCO_2H + SiHCl_3 + R_3N \xrightarrow[\Delta]{CH_3CN} RCH_2SiCl_3 + R_3\overset{+}{N}H\overset{-}{Cl} + (SiCl_2O)_x$$

In a typical experiment, 1 equiv of benzoic acid and 5 equiv of trichlorosilane were dissolved in 100 ml of acetonitrile and refluxed for 1 hr.[4] Two equivalents of tri-*n*-propylamine was added at this point and the resulting mixture was refluxed at 79–86° for 14 hr. Treatment with dry ether caused the precipitation of tri-*n*-propylamine hydrochloride (95%). Distillation of the filtrate gave benzyltrichlorosilane (58%) boiling at 82–84° (8 mm). The pot residue was a resinous material whose ir spectrum was dominated by Si–O absorption at 8.5–9.5 μ. Data for the transformation of a series of aromatic acids are summarized in Table I.

When a mixture of *p*-nitrobenzoic acid, trichlorosilane, and tri-*n*-propylamine was refluxed for 2 hr, a gelatinous colored material was formed which did not contain *p*-nitrobenzyltrichlorosilane. Further work is presently underway to delineate the effects of aromatic substituents on the course of the reaction as well as to ascertain whether it can be extended to aliphatic acids.

Since it is well known that benzylic silanes are readily cleaved by base,[5] the method herein described holds promise as a procedure for converting benzoic acids to substituted toluenes. It has already been shown that the benzyltrichlorosilane resulting from run 1 (Table I) can be cleaved readily to toluene.[6] Further experiments are currently underway in our laboratory to determine the generality and feasibility of such a two-step process for reducing a carboxyl group to methyl.

We must reemphasize that the mechanism of "reductive silylations," such as described here and previously,[3] remains speculative. The current thrust of our program has been directed solely at illustrating the preparative value of the method.

(1) R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, **69**, 2548 (1947); H. C. Brown and B. C. Subba Rao, *ibid.*, **82**, 681 (1960).
(2) R. A. Benkeser and W. E. Smith, *ibid.*, **90**, 5307 (1968).
(3) R. A. Benkeser and W. E. Smith, *ibid.*, **91**, 1556 (1969).
(4) It should be emphasized that the stoichiometry of the reactants has not been ascertained nor any attempt made to optimize reaction conditions.

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(5) C. Eaborn, "Organosilicon Compounds," Butterworth and Co., Ltd., London, 1960, pp 143–146.
(6) Unpublished studies by J. M. Gaul and K. M. Foley of these laboratories.

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Fluxional Behavior in *Tetrahapto*benzene–Rhodium and –Iridium Complexes

Sir:

We report the first example of fluxional behavior in a benzene–metal complex. Fluxional behavior in cyclic π- and σ-bonded organometallic systems, where the metal atom usually moves along the periphery of a ring by a series of 1,2 shifts, is a well-established phenomenon.[1] It has been observed for cyclooctatetraene[1]

(1) This topic has recently been reviewed: F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).