Anal. Calcd for $C_{38}H_{54}O_{16}$: *m/e* 766.3409. Found: *m/e* 766.3400.

**Methanolysis of 16.** This was carried out by a procedure exactly identical with that for the methanolysis of **7**. The methyl 2,3,4,6-tetra-*O*-methyl-$\beta$-D-glucopyranoside isolated was identified by TLC and GLC with the compound prepared from methylation of D-glucose.

**Brucein-D (3).** Brucein-D showed the following: mp 294–296 °C (dichloromethane–ether–methanol) (lit.[10] mp 285–290 °C); IR (Nujol) 3380 (br), 1710, 1655, 1620 $cm^{-1}$; $^{13}C$ NMR (25.20 MHz, $Me_2SO$-$d_6$) 73.0 (C-1), 166.5 (C-2), 107.1 (C-3), 138.6 (C-4), 41.8 (C-5), 29.6 (C-6), 63.1 (C-7), 46.9 (C-8), 42.9 (C-9), 46.1 (C-10), 70.8 (C-11), 71.7 (C-12), 72.6 (C-13), 74.4 (C-14), 66.9 (C-15), 146.9 (C-16), 62.7 (C-17), 25.6 (Me-4), 16.7 (Me-10), 22.6 (Me-13).

Anal. Calcd for $C_{20}H_{26}O_9$: C, 58.53, H, 6.39. Found: C, 58.61; H, 6.39.

**Brucein-D Triacetate (13).** Acetylation of **3** (10 mg) with acetic anhydride (1 mL) and pyridine (1 mL) at room temperature for 46 h followed by the usual workup yielded a product which was purified by preparative TLC (5:1 chloroform–acetone) to give a triacetate [**13**, 8 mg, mp 243–246 °C (ether–chloroform)] whose NMR spectrum (Table I) was in accord with the assigned structure.

Anal. Calcd for $C_{26}H_{32}O_{12}$: C, 58.20; H, 6.01. Found: C, 58.10; H, 6.00.

**Oxidation of 13 with Jones' Reagent.** To a solution of **13** (2.8 mg) in acetone (2 mL) was added one drop of Jones' reagent. After the mixture was kept at room temperature for 3 h, it was diluted with water and the product was extracted with ether. The ether extract was washed, dried, and evaporated to give a ketone (**17**, 2 mg), mp 254–256 °C (acetone–carbon tetrachloride) (lit.[9] mp 259–262 °C). The NMR spectrum of **17** is identical with that of 11-ketobrucein triacetate reported by Polonsky and co-workers.[10]

**Brucein-E (4).** Brucein-E was obtained as colorless crystals (chloroform–methanol–water): mp 261–265 °C (lit.[10] mp 260–264 °C); IR (Nujol) 3500, 3250, 1710, 1660 $cm^{-1}$.

Anal. Calcd for $C_{20}H_{28}O_9$: C, 58.24; H, 6.84. Found: C, 58.56; H, 6.72.

**Brucein-E Tetraacetate (14).** Acetylation of **4** (20 mg) by treatment with acetic anhydride–pyridine yielded a product (13 mg) which gave an NMR spectrum which was consistent with the structure of brucein-E tetraacetate (**14**). The product (**14**) formed colorless needles from ether–chloroform and had mp 250–253 °C (lit.[10] mp 250–254 °C).

Anal. Calcd for $C_{28}H_{36}O_{13}$: C, 57.92; H, 5.79. Found: C, 57.58; H, 5.60.

**Acknowledgments.** This investigation was supported by grants from the National Cancer Institute (CA 17625 and CA 22929) and the American Cancer Society (CH-19) We thank Dr. T. A. Geissman, Department of Chemistry, University of California at Los Angeles, for a gift of brusatol, Dr. Mme. J. Polonsky, Institut de Chimie des Substances Naturelles, Gif-sur-Yvette, France, for authentic samples of brucein-D and -E, Dr. D. L. Harris, Department of Chemistry, University of North Carolina, for $^1H$ NMR spectra, Mr. K. Goto of JEOL Analytical Instruments, Inc., for $^{13}C$ NMR spectra, and Dr. David Rosenthal and Mr. Fred Williams of the Research Triangle Center for Mass Spectrometry for mass spectral data.

**Registry No.**—**1**, 63306-30-9; **2**, 69687-69-0; **3**, 21499-66-1; **4**, 21586-90-3; **5**, 63344-09-2; **6**, 69687-70-3; **7**, 63344-10-5; **8**, 14907-98-3; **8**, 14907-98-3; **9**, 63344-08-1; **10**, 69687-71-4; **11**, 69687-72-5; **12**, 14907-99-4; **13**, 21586-89-0; **14**, 21499-68-3; **16**, 69745-20-6; **17**, 21499-67-2; methyl 2,3,4,6-tetra-*O*-methyl-$\beta$-D-glucopyranoside, 3149-65-3.

## References and Notes

(1) (a) Dedicated to the memory of the late Dr. T. A. Geissman, Professor Emeritus of the Department of Chemistry, University of California at Los Angeles. (b) For part 32, see K.-H. Lee, E. C. Mar, M. Okamoto, and I. H. Hall, *J. Med. Chem.*, **21**, 819 (1978). Presented in part before the Academy of the 125th American Pharmaceutical Association Annual Meeting in Montreal, Canada, May 16, 1978.

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(5) In vivo activity was assayed by the standard National Cancer Institute procedures described by R. I. Geran, N. H. Greenberg, M. M. MacDonald, A. M. Schumacher, and B. J. Abbott, *Cancer Chemother. Rep., Part 3*, **3**, 1 (1972). Bruceoside-A and -B showed significant (T/C ≥ 120%) antileukemic activity in P-388 leukemia (T/C = 156 and 132%) at the 6 and 1.5 mg/kg/day levels, respectively. Brucein-D demosntrated significant inhibitory activity against the Walker 256 carcinosarcoma in rats at T/C 144% at the 0.5 mg/kg/day level.

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(10) J. Polonsky, Z. Baskèvitch, M. B. Das, and J. Müller, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **267**, 1346 (1968).

(11) A voucher specimen is available for inspection at the Herbarium of the Department of Botany, Kaohsiung Medical College, Kaohsiung, Taiwan, Republic of China.

(12) Product of Aldrich Chemical Co., Inc., Milwaukee, Wis.

(13) R. D. Guthrie and J. F. McCarthy, *Adv. Carbohydr. Chem.*, **22**, 11 (1967).

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# Novel Conversion of Aromatic Ester Groups to Methyl. Catalytic Effect of Iodine in Reactions Involving Iodotrimethylsilane

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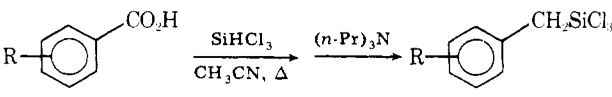
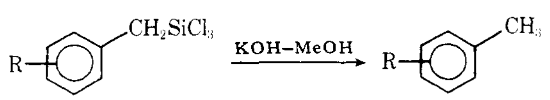
A three-step sequential procedure has been developed whereby a "one-pot" reduction of aromatic ester groups directly to methyl is now possible. One of these steps involves conversion of the aromatic ester to a trimethylsilyloxy ester by means of iodotrimethylsilane or one of its variants. A strong catalytic effect by iodine in reactions involving iodotrimethylsilane has been discovered. The intermediacy of trimethylsilyl triiodide is proposed to explain certain spectral effects noted in the NMR. Iodine catalysis also permits an alternative suggestion as to the reason for the superiority of trimethylphenylsilane–iodine combinations as a substitute for iodotrimethylsilane itself.

Some years ago, we reported[1] that trichlorosilane, in the presence of tertiary aliphatic amines, was a powerful reducing agent. For example, the reagent was capable of reducing aromatic carboxylic acids to benzylic trichlorosilanes[2] (eq 1). The Si–C bond of such benzylic silanes was very susceptible to base cleavage[3] (eq 2). A procedure was devised such that steps 1 and 2 could be carried out sequentially in the same reaction flask,



(1)



(2)

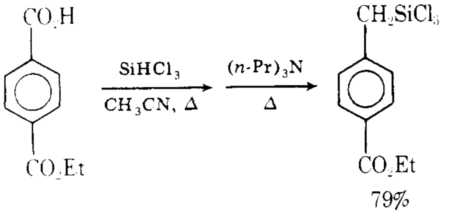
**Table I. Reactions of Various Compounds with Iodotrimethylsilane [a] and Iodotrimethylsilane/$I_2$**

| | compd | cleaving agent | temp, °C | time, h | yield, % NMR [b] | yield, % isolated product |
|---|---|---|---|---|---|---|
| 1 | $C_6H_5CO_2Me$ | $Me_3SiI$ | 110 (50)[c] (100)[d] | 4 (35)[c] (2)[d] | 89 | (85)[c] (80)[d] |
| 2 | $C_6H_5CO_2Me$ | $Me_3SiI/I_2$[e] | 25 | 4 | 100 | 99 |
| 3 | $C_6H_5CO_2Et$ | $Me_3SiI$ | (50)[c] (100)[d] | (48)[c] (4)[d] | (100)[c] | (72)[d] |
| 4 | $C_6H_5CO_2Et$ | $Me_3SiI/I_2$[e] | 25 | 8 | 100 | |
| 5 | $C_6H_{11}OSiMe_3$ | $Me_3SiI$ | 50 (25)[f] | 24 (24)[f] | | 98 (75)[f] |
| 6 | $C_6H_{11}OSiMe_3$ | $Me_3SiI/I_2$[e] | 50 | 3 | | 100 |
| 7 | $C_6H_5CH_2CO_2Et$ | $Me_3SiI$ | (100)[d] | (4)[d] | | (70)[d] |
| 8 | $C_6H_5CH_2CO_2Et$ | $Me_3SiI/I_2$[e] | 100 | 0.33 | 100 | 90 |
| 9 | $(CH_3)_3CCO_2Me$ | $Me_3SiI$ | (100)[d] | (18)[d] | | (55)[d] |
| 10 | $(CH_3)_3CCO_2Me$ | $Me_3SiI/I_2$[e] | 85 | 3 | 97 | 93 |
| 11 | $p$-$CH_3C_6H_4CO_2Me$ | $Me_3SiI/I_2$[e] | 25 | 4 | 97 | 93 |
| 12 | $p$-$CH_3OC_6H_4CO_2Me$ | $Me_3SiI/I_2$[e] | 50 | 3 | | 86 |
| 13 | $C_6H_{11}OH$ | $Me_3SiI$[g] | 50 | 5 | | 46 |

[a] Values in parentheses are results reported by authors indicated in these footnotes. Values not in parentheses are from this work. [b] The NMR yield was obtained by integration of the –OR protons (disappearance) and the RI protons (appearance) where appropriate. [c] M. E. Jung and M. A. Lyster, *J. Am. Chem. Soc.*, **99**, 968 (1977). [d] T-L. Ho and G. A. Olah, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 4 (1978). [e] 10 mol % of iodine (based on substrate) was used. [f] M. E. Jung and P. J. Ornstein, *Tetrahedron Lett.*, 2659 (1977). The product of this reaction is cyclohexyl iodide. [g] 2 equiv of $Me_3SiI$ was used here. The product of the reaction is cyclohexyl iodide.

thereby providing a "one-pot" method for reducing aromatic carboxyl groups to methyl.[4]

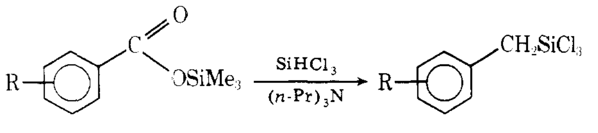
The trichlorosilane–tertiary amine combination proved strangely unreactive toward ordinary aromatic ester groups. Perhaps the most graphic demonstration of this fact was that carboxyl groups could be reduced in the presence[5] of ester groups as shown in eq 3. This was indeed an anomaly since simple ester groups are generally much easier to reduce than carboxyl groups.[6]



(3)

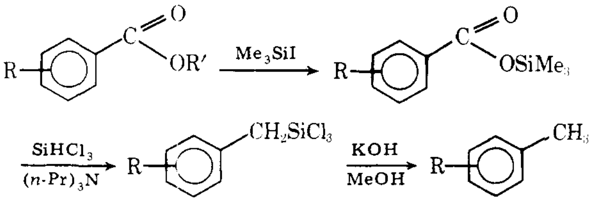
In the procedure developed to reduce carboxyl groups, the aromatic acid was first heated with trichlorosilane in acetonitrile for about 1 h *before* the amine was added (eq 1). During this 1-h interval, the evolution of HCl gas was evident. This proved to be an important observation since it would seem that the moiety undergoing reduction was not the carboxylic acid itself, but rather some silyloxy ester of the acid.

We can now report that a wide variety[7] of trimethylsilyl benzoate esters can be reduced successfully with the trichlorosilane–tertiary amine combination in accord with eq 4. Why silicon esters undergo reduction when other ester groups are resistant will be the subject of a later paper.



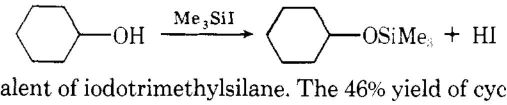
(4)

The advent of iodotrimethylsilane[8] as a convenient and mild reagent for converting aromatic esters to trimethylsilyl esters provided us with a vital tool in developing the three-step sequential procedure depicted in eq 5.



(5)

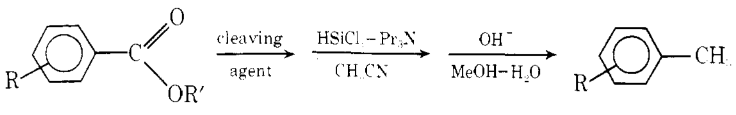
In any multistep synthesis of this type it behooves one to develop procedures such that each step proceeds in the highest yield possible. In the course of carrying out reactions with iodotrimethylsilane in step 1 of eq 5, we discovered that the presence of 10 mol % of iodine (based upon the substrate to be cleaved) catalyzed the reactions markedly, so that they usually proceeded more rapidly and under milder conditions. This can be seen by comparing the first ten entries of Table I. This table lists all of the compounds (esters, alcohols, or their trimethylsilyl ethers) which we treated with iodotrimethylsilane both in the presence or absence of catalytic amounts of iodine. Incorporated into Table I are also the results of other workers who used the same substrates as we but in the absence of iodine. The beneficial effects of the iodine are quite apparent. Table II shows the wide variety of esters that were reduced to methyl compounds in accord with eq 5. It should be noted that this three-step reduction sequence frequently gave overall yields greater than 50%. One might argue that traces of HI in the iodotrimethylsilane were responsible for the results in Table I. While this cannot be totally discounted, entries 6 and 13 in the table would militate against the idea. In entry 13, *2* equiv of iodotrimethylsilane was used for each equivalent of cyclohexanol. Certainly the first equivalent of the iodotrimethylsilane would react to produce (cyclohexyloxy)trimethylsilane and *1* equiv of HI (eq 6). The latter would be in the presence of the remaining equivalent of iodotrimethylsilane. The 46% yield of cyclohexyl iodide would certainly not indicate any beneficial effects of HI, especially when compared with the results of entry 6. In the latter case, a quantitative yield of cyclohexyl iodide was realized under essentially the same conditions of time and temperature as entry 13.



(6)

The degree of completion of the reaction with iodotrimethylsilane (step 1 of eq 5) and the carboxylic esters could be followed very conveniently by NMR. One could compare the peak areas resulting from the –OR protons in the starting ester to those for the alkyl iodide product. The area of the singlet which appeared for the protons in the trimethylsilyl ester product, $-OSiMe_3$ ($\delta$ 0.44), could also be used. The validity of the NMR method of analysis was checked in several cases by actually *isolating the trimethylsilyl ester product*. Invariably, the agreement was quite good as indicated in Table I.

**Table II. Conversion of Aromatic Ester Groups to Methyl**



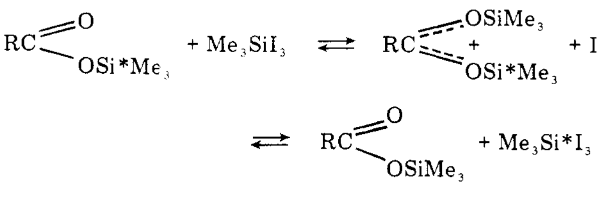
| | R | R′ | cleaving agent | cleavage time, h | cleavage temp, °C | yield of reduced product, % |
|---|---|---|---|---|---|---|
| 1 | H | Me | $Me_3SiI$ | 5 | 50 | 28 |
| 2 | H | Me | $C_6H_5SiMe_3/I_2$[d] | 4 | 107 | 67 |
| 3 | H | Et | $C_6H_5SiMe_3/I_2$[d] | 4 | 110 | 66 |
| 4 | *o*-Me | Et | $C_6H_5SiMe_3/I_2$[d] | 4.5 | 115 | 64 |
| 5 | *p*-Me | Et | $C_6H_5SiMe_3/I_2$[d] | 5 | 110 | 59 |
| 6 | H | Me | $Me_3SiI$[a] | 4 | 110 | 68 |
| 7 | H | Me | $Me_3SiI/I_2$[e] | 4 | 25 | 68 |
| 8 | *p*-Me | Me | $Me_3SiI/I_2$[e] | 5 | 25 | 65 |
| 9 | *o*-Me | Me | $Me_3SiI/I_2$[e] | 5 | 25 | 70 |
| 10 | *p*-MeO | Me | $Me_3SiI/I_2$[e] | 20 | 25 | 36 |
| 11 | *p*-MeO | *t*-Bu | $Me_3SiI/I_2$[e] | 1 | 25 | 36 |
| 12 | *o*-$C_6H_5C(=O)$– | Me | $Me_3SiI/I_2$[e] | 5 | 7 | 56[b] |
| 13 | *p*-$(CH_3)_2N$– | Et | $Me_3SiI/I_2$[e] | 4 | 100 | 54[c] |

[a] Iodotrimethylsilane was prepared from $C_6H_5SiMe_3$ and $I_2$ at 100 °C and distilled directly into the reaction flask. [b] The yield is of the completely reduced product, phenyl(*o*-tolyl)methane. [c] The yield given is comprised of two products, *N*,*N*-dimethyl-*p*-toluidine (71%) and *N*-ethyl-*N*-methyl-*p*-toluidine (16%). [d] 1.2 equiv of iodine was used. [e] 10 mol % of iodine was used.

Significantly, when about 3 mg of iodine was added to the reaction mixture consisting of iodotrimethylsilane and the carboxylic ester, the two trimethylsilyl peaks (from iodotrimethylsilane and the $-OSiMe_3$ of the silyl ester product) coalesced into one broad peak centered at $\delta$ 0.48. This clearly indicated that the iodine was providing a pathway for a rapid exchange of the trimethylsilyl groups of iodotrimethylsilane and the trimethylsilyl ester. We have not investigated how this exchange is occurring, but one possibility is that the iodine sets up an equilibrium with the iodotrimethylsilane to form a small amount of trimethylsilyl triiodide (eq 7). The triiodide–silicon

$$Me_3SiI + I_2 \rightleftharpoons Me_3i^{\delta+}I_3{}^{\delta-} \qquad (7)$$

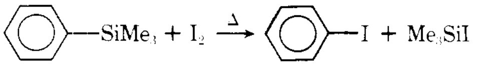
bond would be expected to be more polarizable than the silicon–iodine bond in iodotrimethylsilane. Even though the triiodide was present in low concentrations, it might well effect a facile exchange with the trimethylsilyl ester (eq 8). In those



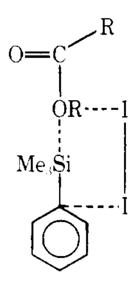
$$RC(=O)OSi^*Me_3 + Me_3SiI_3 \rightleftharpoons RC(\overset{+}{\cdots}OSiMe_3)(\cdots OSi^*Me_3) + I_3{}^- \rightleftharpoons RC(=O)OSiMe_3 + Me_3Si^*I_3 \qquad (8)$$

cases where the reaction was carried out with iodotrimethylsilane, the carboxylic ester, and 10 mol % of iodine, only one trimethylsilyl peak was observed in the NMR throughout the reaction. Initially it was very broad, but it sharpened and shifted upfield as the reaction progressed.

The observation that iodine exerts a catalytic effect in cleavage reactions involving iodotrimethylsilane provides an attractive alternative explanation as to why a phenyltrimethylsilane–iodine mixture is a more effective cleaving agent than preformed iodotrimethylsilane itself. The present explanation[9] is that a six-membered transition state (I) is involved rather than the in situ formation of iodotrimethylsilane from the cleavage of phenyltrimethylsilane with iodine[10] (eq 9).

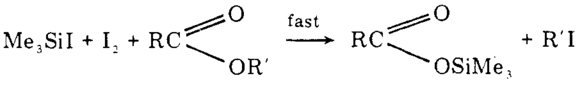


(9)



I

We have corroborated the claim[9] that phenyltrimethylsilane–iodine is superior to iodotrimethylsilane alone, particularly in the rate of formation and the overall yield of the trimethylsilyloxy ester. However, the experimental directions[9] for the phenyltrimethylsilane–iodine reactions call for a 12 mol % excess of iodine[9b] over and above that required by the stoichiometry of eq 9. Hence, if iodotrimethylsilane were formed in accord with eq 9, it would be in the presence of excess iodine. The trimethylsilyl iodide would thus enjoy the catalytic effects of iodine which we have found, and increased reaction rates would result in accord with eq 10. We are thus proposing that the phenyltrimethylsilane–iodine method[9] does *not* involve a six-membered transition state (I) but rather proceeds via iodotrimethylsilane generated as depicted in eq 9. The increase in rate is the result of the catalytic effect of iodine.



$$Me_3SiI + I_2 + RC(=O)OR' \xrightarrow{\text{fast}} RC(=O)OSiMe_3 + R'I \qquad (10)$$

There is at least one difficulty to be resolved if iodotrimethylsilane is to be postulated as an intermediate in the iodine cleavage of phenyltrimethylsilane (eq 9). Iodotrimethylsilane was first prepared[10] by Whitmore et al. by the method of eq 9. Equimolar quantities of phenyltrimethylsilane and iodine were used, and the mixture was refluxed for 12 h in the absence of any solvent. From the boiling point of phenyltrimethylsilane, one might judge that the reaction temperature must have been in the vicinity of 170 °C. Only a 56% yield of iodotrimethylsilane was reported by this method. It would seem that the "Whitmore" reaction was slow and required vigorous conditions. If such were the case, it could not explain the very rapid and high yield reactions which are realized in the phenyltrimethylsilane–iodine conversions of carboxylic esters to the trimethylsilyloxy esters. Accordingly, we repeated the Whitmore reaction[10] employing a 12 mol % excess of iodine and a reaction temperature of only 110 °C (the same temperature used in ref 9). After 30 min, analysis by VPC indicated that all of the phenyltrimethylsilane had disappeared and that the cleavage was complete. An NMR spectrum of the mixture at this point showed only a sharp singlet at $\delta$ 0.85 (iodotrimethylsilane) and aromatic peaks resulting from the iodobenzene. In a larger run, but using the same mole ratios of phenyltrimethylsilane and iodine, an isolated yield of 63% of iodotrimethylsilane was obtained in 45 min. It is eminently clear that the vigorous conditions employed by Whitmore are unnecessary in the presence of excess iodine.

## Experimental Section

**Starting Materials.** Trimethylsilyl benzoate was prepared in 97% yield from benzoic acid and hexamethyldisilazane.[11] Phenyltrimethylsilane was prepared from phenylmagnesium bromide and trimethylchlorosilane (Aldrich). Iodotrimethylsilane was prepared in 75% yield by the method of Jung.[12] The esters were either purchased or prepared by classical procedures. Tri-*n*-propylamine (Aldrich) was dried by pretreatment with sodium hydroxide, followed by distillation from barium oxide. It was stored over 4 Å molecular sieves. Trichlorosilane (Aldrich) was distilled from quinoline and stored under dry nitrogen in the cold. Acetonitrile was distilled from $P_2O_5$ and stored over 3 Å molecular sieves.

**Reductive Silylation of Trimethylsilyl Benzoate.** Trimethylsilyl benzoate (19.4 g, 0.1 mol) and trichlorosilane (30.0 mL, 0.3 mol) were placed in a flame-dried flask. This solution was cooled in ice while tri-*n*-propylamine (28.6 g, 0.2 mol) was slowly added (1.5 h). When this addition was completed, the mixture was heated to reflux (~75 °C) for 20 h. It was then added to 1 L of anhydrous ether, and the amine hydrochloride which precipitated was filtered. The ether was distilled, followed by removal of the volatiles at reduced pressure (40 °C at 80 mm). The residue was distilled to afford one fraction: 15.2 g; bp 85 °C (5 mm) to 100 °C (1 mm). The major portion distilled between 85 and 90 °C at 5 mm.

Analysis by VPC (SE-30, 220 °C) indicated only two components (ratio of 82:18): benzyltrichlorosilane[13] (55% yield) and $\alpha,\alpha$-bis(trichlorosilyl)toluene[14] (7% yield).

**Modified Procedure for Reactions with Iodotrimethylsilane.** The carboxylic ester, alcohol, or trimethylsilyl ether was combined with 1.2 equiv of iodotrimethylsilane and approximately 10 mol % of iodine (based on the ester, alcohol, or ether) in a flame-dried flask. The mixture was heated to the desired temperature for the appropriate time (see Tables I and II). NMR analysis was used to judge the completion of the reaction. The mixture was quenched with water, taken up in ether or chloroform, and deiodinated, and the organic extracts were dried. Removal of the solvent afforded the product.

In a typical experiment, methyl benzoate (5.44 g, 40 mmol), iodotrimethylsilane (6.7 mL, 9.6 g, 48 mmol), and iodine (1.0 g, 4 mmol) were allowed to react for 4 h at room temperature. The mixture was poured into 30 mL of water, treated with $Na_2S_2O_3$ (aqueous) to remove the iodine, and extracted with 3 × 25 mL of $CHCl_3$. The extracts were washed with saturated aqueous NaCl and dried ($Na_2SO_4$), and the solvent was removed. The yield of pure benzoic acid was 4.85 g (99%), mp 120–121 °C (example 2, Table I).

**Conversion of an Aromatic Ester Group to Methyl. General Procedure.** The aryl ester (0.1 mol) and the cleaving agent (0.12 mol) were combined in a flame-dried 300-mL flask. The mixture was heated to the desired temperature (or stirred at room temperature) until the reaction was complete (NMR). It was then dissolved in 80 mL of acetonitrile, and 30 mL (0.3 mol) of $SiHCl_3$ was added. The mixture was cooled (0 °C), and tri-*n*-propylamine was added slowly. After the amine was added, the mixture was heated to reflux for 20 h. It was then taken up in 1 L of anhydrous ether and cooled to 0 °C for several hours. The amine hydrochloride which had precipitated was filtered off and the ether distilled. The volatiles were removed under reduced pressure. The residue was treated under reflux with 50 mL of methanol. After 1 h the solution was cooled and 59.1 g of KOH dissolved in 95 mL of methanol and 25 mL of water was added. The mixture was again heated to reflux for 24 h and then poured into 600 mL of water. The organic layer was extracted with pentane, and the latter was neutralized by shaking with 5 N HCl. The extracts were dried ($Na_2SO_4$) and the pentane was removed through a 15-cm Vigreux column. The product was obtained by distilling the residue through a short-path distilling head (see Table II).

**Effect of Iodine on the NMR Spectrum of Iodotrimethylsilane Cleavages.** Methyl benzoate (2.7 g, 20 mmol) and iodotrimethylsilane (3.4 mL, 4.8 g, 24 mmol) were combined and heated to 110 °C. After 2 h an aliquot was removed and analyzed by NMR. The reaction was partially complete (83%) as determined by the presence of peaks for both methyl iodide and methyl benzoate ($-OCH_3$). The relative completion was determined by integration of the two peaks. Also observed were peaks corresponding to the products, trimethylsilyl benzoate ($-OSiMe_3$) at $\delta$ 0.44 and iodotrimethylsilane at $\delta$ 0.84. At this point, about 3 mg of $I_2$ was placed in the tube. Immediately, the two trimethylsilyl peaks coalesced into one broad peak with a shoulder, centered at $\delta$ 0.58.

In those cases where the cleavage was carried out with iodotrimethylsilane and 10 mol % iodine, only one trimethylsilyl peak was observed throughout the course of the reaction. Initially it was very broad, but it sharpened and shifted upfield as the reaction progressed.

**Phenyltrimethylsilane and Iodine.** Phenyltrimethylsilane (1 g, 6.7 mmol) and iodine (1.91 g, 7.5 mmol) were allowed to react in a 10-mL, two-neck flask equipped with a rubber septum and condenser at 110 °C in a nitrogen atmosphere. Aliquots were taken and analyzed by VPC (12 ft × 1/4 in. 10% QF-1 on Chrom G at 145 °C). After 30 min, the phenyltrimethylsilane had disappeared and a new peak identified as iodobenzene had appeared along with iodotrimethylsilane. This NMR spectrum of the product showed a sharp singlet at $\delta$ 0.85 (iodotrimethylsilane) plus aromatic peaks for iodobenzene.

In a larger run, phenyltrimethylsilane (5 g, 34 mmol) and iodine (9.55 g, 38 mmol) were allowed to react at 115 °C in a 50-mL flask equipped with a short-path distillation head. After 45 min, 4.3 g of distillate was collected boiling at 95–100 °C. NMR showed this to be 98% pure iodotrimethylsilane in a 63% yield.

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**Registry No.**—$C_6H_5Co_2Me$, 93-58-3; $C_6H_5Co_2Et$, 93-89-0; $C_6H_{11}OSiMe_3$, 13871-89-1; $C_6H_5CH_2CO_2Et$, 101-97-3; $(CH_3)_3CCO_2Me$, 598-98-1; *p*-$CH_3C_6H_4CO_2Me$, 99-75-2; $C_6H_{11}OH$, 108-93-0; *o*-$CH_3C_6H_4CO_2Et$, 87-24-1; *p*-$CH_3C_6H_4CO_2Et$, 94-08-6; *o*-$CH_3C_6H_4CO_2Me$, 89-71-4; *p*-$CH_3OC_6H_4CO_2$-*t*-Bu, 833-79-4; *o*-$C_6H_5COC_6H_4CO_2Me$, 606-28-0; *p*-$(CH_3)_2NC_6H_4CO_2Et$, 10287-53-3; $C_6H_5CH_3$, 108-88-3; *p*-$CH_3OC_6H_4CO_2Me$, 121-98-2; $C_6H_{11}I$, 626-62-0; $C_6H_5CH_2CH_3$, 100-41-4; $(CH_3)_3CCH_3$, 463-82-1; *p*-$CH_3C_6H_4CH_3$, 106-42-3; *o*-$CH_3C_6H_4CH_3$, 95-47-6; *p*-$CH_3OC_6H_4CH_3$, 104-93-8; *o*-$C_6H_5COC_6H_4CH_3$, 131-58-8; *p*-$(CH_3)_2NC_6H_4CH_3$, 99-97-8; *p*-$CH_3(C_2H_5)NC_6H_4CH_3$, 35113-87-2; $Me_3SiI$, 16029-98-4; trimethylsilyl benzoate, 2078-12-8; $SiHCl_3$, 10025-78-2; benzyltrichlorosilane, 770-10-5; $\alpha,\alpha$-bis(trichlorosilyl)toluene, 23487-33-4; $PhSiMe_3$, 768-32-1; $I_2$, 7553-56-2.

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