Anal. Calcd for $C_{11}H_{18}OSSi$: C, 58.36; H, 8.01; S, 14.16. Found: C, 58.52; H, 7.79; S, 14.31.

Registry No.—**1d**, 40110-24-5; **4**, 18789-72-5; *cis*-**6a**, 40110-65-4; *trans*-**6a**, 40110-66-5; **6b**, 40110-26-7; **6c**, 40110-27-8; *cis*-**6d**, 40110-67-6; *trans*-**6d**, 40110-68-7; *trans*-**6e**, 40110-69-8; *cis*-**6e**, 40110-70-1; *cis*-**6f**, 40110-71-2; *trans*-**6f**, 40110-72-3; **6g**, 40110-28-9; **6h**, 40110-29-0; **7**, 23975-23-7; **8**, 23975-27-1; **10**, 40110-32-5; **12**, 21147-11-5; **13**, 40110-34-7; **15**, 6099-23-6; **16**, 40110-36-9; **17**, 40110-37-0; benzaldehyde, 100-52-7; adamantanone, 700-58-3; cyclohexanone, 108-94-1; acrolein, 107-02-8; *trans*-cinnamaldehyde, 14371-10-9; cyclohexenone, 930-68-7; 1-trimethylsilyl-1-(methylsulfinyl)methyllithium, 40110-38-1; benzophenone, 119-61-9; dimethyl sulfoxide 67-68-5; trimethylchlorosilane, 75-77-4; methyl phenyl sulfoxide, 1193-82-4; ethyl benzoate, 93-89-0.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Silane Reductions in Acidic Media. II. Reductions of Aryl Aldehydes and Ketones by Trialkylsilanes in Trifluoroacetic Acid. A Selective Method for Converting the Carbonyl Group to Methylene[1a,b]

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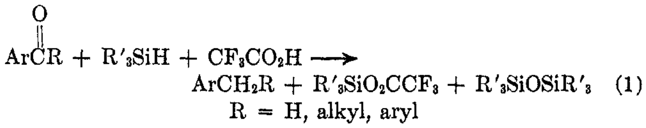
Trialkylsilanes in trifluoroacetic acid media selectively reduce the carbonyl group of arylcarbonyl compounds to methylene. Aryl alkyl ketones and diaryl ketones that can be synthesized by Friedel–Crafts acylation procedures are quantitatively reduced to the corresponding arenes. Benzaldehydes substituted with activating groups form the corresponding toluenes; however, substituted toluene formation is competitive with Friedel–Crafts alkylation. Specific γ-lactone formation occurs in the reduction of 3-benzoylpropanoic and *o*-benzoylbenzoic acids. The requirements and limitations of trialkylsilane reductions have been examined and procedures for the isolation of arene products determined.

The reduction of the carbonyl group of aldehydes and ketones to methylene has enjoyed wide application in organic syntheses. Of the reductive methods that have been employed, the Clemmensen[2] and Wolff–Kishner[3] reactions have exhibited the most general utility. Other methods, including catalytic hydrogenation,[4] reductions using Raney nickel in hydroxide media,[5] and trichlorosilane–trialkylamine[6] and metal hydride reductions,[7] have been successfully applied more specifically to aryl aldehydes and ketones.

Kursanov, Parnes, and coworkers have recently reported the reduction of the carbonyl group of benzophenone, Michler's ketone, acetophenone, and 2,4,6-trimethylbenzaldehyde to methylene using triethylsilane in trifluoroacetic acid media.[8] Because of the good yields reported for these silane reductions and the reported ability of silanes to undergo hydride transfer to relatively stable carbenium ions,[9,10] we expected that silane reductions of aldehydes and ketones would represent a convenient and synthetically useful method for transforming a carbonyl group to methylene. In this paper we report the application of trialkylsilanes to reductions of aryl aldehydes and ketones in acidic media.

Results

The yields of arylhydrocarbon products from trialkylsilane reductions of the corresponding carbonyl compounds are given in Table I. In general, 2 equiv of silane are required for the reduction of 1 equiv of carbonyl compound to the methylene product in trifluoroacetic acid (eq 1); silane products are the trialkylsilyl trifluoroacetate and hexaalkyldisiloxane in amounts that vary with the reaction conditions. Reductions were observed to occur readily at room temperature and for phenyl alkyl ketones and diaryl ketones generally required less than 15 min for complete reduction. Reductions of aliphatic aldehydes and ketones, such as octanal and cyclohexanone, did not give the corresponding methylene products.



$$\mathrm{Ar\overset{\overset{O}{\|}}{C}R + R'_3SiH + CF_3CO_2H \longrightarrow ArCH_2R + R'_3SiO_2CCF_3 + R'_3SiOSiR'_3} \qquad (1)$$

$R = H$, alkyl, aryl

Trifluoroacetic acid was chosen as the solvent for these reactions because of its acidity and good solvat-

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[1] (a) Support for this work from the Research Corporation is gratefully acknowledged. (b) Part I: M. P. Doyle, D. J. DeBruyn, and D. A. Kooistra, *J. Amer. Chem. Soc.*, **94**, 3659 (1972). (c) National Science Foundation Undergraduate Research Participant, summer 1971.

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TABLE I

SILANE REDUCTIONS OF ARYLCARBONYL COMPOUNDS IN TRIFLUOROACETIC ACID MEDIA[a]

Registry no.	Carbonyl compound	Solvent	Equiv CF_3CO_2H[b]	Equiv $R_3{}^1SiH$[b,c]	Reaction time, hr[d]	Yield of $ArCH_2R$, %[e]
487-68-3	2,4,6-Trimethylbenzaldehyde	CF_3CO_2H	10.0	2.2	0.25	98
123-11-5	*p*-Anisaldehyde[f]	CF_3CO_2H	5.0	2.5[f]	0.50	76
		CF_3CO_2H[h]	5.0	6.0[g]	1.50	80
		CF_3CO_2H	5.0	6.0[g]	0.50	81
		CF_3CO_2H	5.0	6.0	0.75	83
104-87-0	*p*-Tolualdehyde	CF_3CO_2H	8.0	2.2	11	20
		CF_3CO_2H	8.0	2.2[g]	13	46
		CF_3CO_2H	5.0	2.5[g]	0.25	52
		CH_3CN (2.5 ml)–CF_3CO_2H[i,j]	5.0	6.0	170	50
		CH_3CN (2.5 ml)–CF_3CO_2H[h,i]	6.7	2.2	180	43
		CH_3NO_2 (2.5 ml)–CF_3CO_2H[i]	5.0	6.0	54	61
		CCl_4 (2.5 ml)–CF_3CO_2H[i]	5.0	2.2	100	50
		CCl_4 (2.5 ml)–CF_3CO_2H[i]	5.0	6.0	336	66
98-86-2	Acetophenone	CF_3CO_2H	10.0	2.2	0.25	100
		CF_3CO_2H	3.3	1.0	0.50	50[k]
		CF_3CO_2H	6.8	4.4[l]	44	91
93-55-0	Propiophenone	CF_3CO_2H	5.4	2.5	0.25	100
495-40-9	Butyrophenone	CF_3CO_2H	10.0	2.2	0.25	100
611-70-1	Isobutyrophenone	CF_3CO_2H	5.4	2.5	0.25	100
1009-14-9	Valerophenone	CF_3CO_2H	10.0	2.2	0.25	100
4433-30-1	Undecanophenone	CF_3CO_2H	10.0	2.2	0.25	100
3375-38-0	1,4-Dibenzoylbutane	CF_3CO_2H	9.0	4.4	19	100
99-91-2	*p*-Chloroacetophenone	CF_3CO_2H	6.7	2.2	200	100
779-90-8	1,3,5-Triacetylbenzene	CF_3CO_2H[m]	12.0	6.6	72	100
529-34-0	α-Tetralone	CF_3CO_2H	8.0	2.2	2.5	100
70-11-1	α-Bromoacetophenone	CF_3CO_2H	7.0	4.4	44	93[n]
1501-05-9	4-Benzoylbutanoic acid	CF_3CO_2H	6.5	2.2	48	100
		CF_3CO_2H	6.5	1.1	12	50[k]
4144-62-1	5-Benzoylpentanoic acid	CF_3CO_2H	7.0	2.4	5.5	100
		CF_3CO_2H	7.0	1.1	20	50[k]
3481-02-5	Phenyl cyclopropyl ketone	H_2O (0.3 ml)–CF_3CO_2H	9.5	2.6	7.0	48[o]
		CCl_4 (2.5 ml)–CF_3CO_2H	5.0	2.2	22	25[p]
		CF_3CO_2H	10.0	2.5	3.5	27[q]
5407-98-7	Phenyl cyclobutyl ketone	H_2O (0.3 ml)–CF_3CO_2H	9.9	2.2	6.0	25
		CCl_4 (2.5 ml)–CF_3CO_2H	5.0	5.0	7.5	26
119-61-9	Benzophenone	CF_3CO_2H	15.0	2.2	0.25	100
		CF_3CO_2H	15.0	1.0	0.25	50[k]
611-95-0	4-Benzoylbenzoic acid	CCl_4 (7.0 ml)–CF_3CO_2H	7.7	3.0	120	100
1144-74-7	4-Nitrobenzophenone	CF_3CO_2H	6.7	2.4	47	100

[a] Reductions were usually carried out at room temperature by adding triethylsilane to a trifluoroacetic acid solution containing the carbonyl compound (5.0 mmol). [b] With respect to carbonyl compound. [c] Unless noted otherwise, triethylsilane was used. [d] Time of analysis; does not necessarily reflect required reaction times. Reactions were continued until no further reduction by silane could be observed. [e] Yield based on pmr analysis of products prior to work-up. Reproducibility was ±2%. [f] Aldehyde in trifluoroacetic acid was added to silane. [g] Phenyldimethylsilane. [h] Reaction performed at 0°. [i] Aldehyde added to silane in acidic media. [j] Reaction run at 55°. [k] Only unreacted starting material (50%) remained. [l] Chlorodimethylsilane. [m] Reaction carried out at 65°. [n] Reaction run at 80°. [o] Aqueous trifluoroacetic acid was added to a stirred solution of triethylsilane and phenyl cyclopropyl ketone at 0°. Yield is based on the amount of reduced material; 25% of starting material remained after 7 hr reaction time. [p] Observed yield; 50% unreacted ketone is present. After 1 week 18% of unreacted ketone, 5% of phenylcyclopropylmethane, and 47% of 1-phenyl-2-butyl trifluoroacetate were observed. [q] 8% unreacted ketone remained.

ing properties. Other acids, including sulfuric acid and antimony pentafluoride, reacted with the trialkylsilane.[11] Aqueous acids were not used because of the insolubility of the silane and carbonyl compounds in these media. When the silane was rapidly added to a trifluoroacetic acid solution containing the carbonyl compound, a reaction occurred that was demonstrably exothermic. A nonhydroxylic solvent, such as carbon tetrachloride, acetonitrile, or nitromethane, was used in specific cases to moderate the reaction temperature during the addition of the silane or to facilitate the homogeneity of the solution. With the exception of the reaction between 4-benzoylbenzoic acid and triethylsilane in trifluoroacetic acid–nitromethane, all reaction solutions reported in Table I were homogeneous. During the reduction of 4-benzoylbenzoic acid an insoluble white solid formed; the use of carbon tetrachloride as a cosolvent eliminated this problem. The use of a cosolvent, however, noticeably increased the reaction time for complete reduction.

Under similar conditions, triethyl-, tri-*n*-propyl-, tri-*n*-butyl-, and tri-*n*-hexylsilane quantitatively reduced acetophenone to ethylbenzene without significant differences in reaction times. Chlorodimethylsilane, however, slowly reacted with trifluoroacetic acid and was observed to undergo a minor competing reaction to form a silyl ether of 1-phenylethanol. Trihexylsilane was only partially soluble in trifluoroacetic acid.

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[11] The oxidation of triethylsilane in acidic media has been studied: H. H. Anderson, *J. Amer. Chem. Soc.*, **80**, 5083 (1958).

With the exception of reactions performed in trifluoroacetic acid–nonhydroxylic solvent mixtures and of reductions of *p*-chloroacetophenone, α-bromoacetophenone, 1,3,5-triacetylbenzene, and 4-nitrobenzophenone, trialkylsilane reductions of the carbonyl compounds listed in Table I were rapid. Aryl alkyl ketones and diaryl ketones were quantitatively converted to the corresponding methylene compound.

2,4,6-Trimethylbenzaldehyde was converted to isodurene in 98% yield; only 2% of the Friedel–Crafts alkylation product previously observed by Kursanov and coworkers under similar reaction conditions[12] was obtained. Friedel–Crafts alkylation became increasingly important in reductions of *p*-anisaldehyde and *p*-tolualdehyde by trialkylsilanes. Neither changing the reducing agent from triethylsilane to phenyldimethylsilane, increasing the amount of initially added silane threefold, nor running the reaction at 0° had a significant effect on the yield of *p*-methylanisole. However, the use of phenyldimethylsilane was preferred over triethylsilane for the reduction of *p*-tolualdehyde in trifluoroacetic acid, and the addition of a cosolvent, particularly nitromethane and carbon tetrachloride, led to a minimization of the competing Friedel–Crafts alkylation process. Here again, the reaction temperature had no significant effect on the ratio of the competing reactions, and a threefold increase in the silane concentration did not have the expected effect of eliminating the Friedel–Crafts alkylation reaction. Both vanillin and salicylaldehyde gave reaction products that could be explained by exclusive Friedel–Crafts alkylation; neither *o*-cresol nor 2-methoxy-4-methylphenol was observed.

The reduction of *p*-tolualdehyde by trialkylsilanes in trifluoroacetic acid media proceeded stepwise to initially yield the trifluoroacetate and symmetrical ether derivatives of *p*-toluyl alcohol, followed by the conversion of these products to *p*-xylene and Friedel–Crafts products (eq 2 and 3). The yields of these

$$p\text{-}CH_3C_6H_4CHO \xrightarrow[CF_3CO_2H]{R'_3SiH} \underset{\text{I}}{p\text{-}CH_3C_6H_4CH_2O_2CCF_3} + \underset{\text{II}}{(p\text{-}CH_3C_6H_4CH_2)_2O} \quad (2)$$

$$\text{I} + \text{II} \xrightarrow[CF_3CO_2H]{R'_3SiH} p\text{-}CH_3C_6H_4CH_3 + \text{Friedel–Crafts products} \quad (3)$$

products with time for the reduction of *p*-tolualdehyde by triethylsilane in trifluoroacetic acid–carbon tetrachloride are presented in Table II. These data indicate that *p*-xylene is produced predominantly by reduction of *p*-toluyl trifluoroacetate and that the symmetrical ether is slowly converted to the trifluoroacetate.[13] Friedel–Crafts alkylation occurs only after all of the *p*-tolualdehyde has been reduced to *p*-toluyl alcohol derivatives and after approximately 25% of *p*-xylene has been produced. Similar results were observed for reductions of *p*-tolualdehyde in other trifluoroacetic acid media and for reductions of *p*-chloroacetophenone, 1,3,5-triacetylbenzene, and α-bromoacetophenone. For these compounds reduction to the arene is much slower than reduction to the alcohol derivative. The relative yields of trifluoroacetate and ether varied with reaction conditions and with each carbonyl compound. Generally, ketones did not give appreciable yields of symmetrical ethers under these conditions.

TABLE II

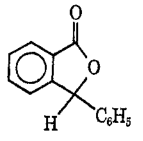
YIELDS OF PRODUCTS FROM THE REDUCTION OF *p*-TOLUALDEHYDE BY TRIETHYLSILANE IN TRIFLUOROACETIC ACID–CARBON TETRACHLORIDE[a]

Time, hr[b]	Trifluoroacetate (I), %	Ether (II), %[c]	*p*-Xylene, %	Friedel-Crafts products, %
16	31	56	13	0
22	31	46	23	0
45	42	30	26	2
89	38	12	39	11
209	9	0	61	30
336	0	0	66	34

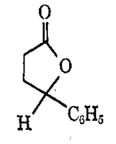
[a] *p*-Tolualdehyde (5.0 mmol) was added to triethylsilane (30.0 mmol) in a constantly stirred solution of trifluoroacetic acid (25.0 mmol) and carbon tetrachloride (2.5 ml) at 25°. Yields were obtained by pmr spectroscopy through reference to an internal standard. [b] No *p*-tolualdehyde was observed at 16 hr reaction time. [c] Per cent of *p*-tolualdehyde that yielded ether.

No trifluoroacetates or symmetrical ethers were observed during the reductions of *p*-anisaldehyde and of aryl alkyl or diaryl ketones. When only 1 equiv of trialkylsilane was used in the reductions of acetophenone and benzophenone, only the corresponding methylene compound (50%) and ketone (50%) were obtained. Even with substituted benzophenones, *p*-nitrobenzophenone and *p*-benzoylbenzoic acid, that required long reaction times for complete reduction, no alcohol derivatives were observed. For these compounds reduction to the arene is faster than the initial reduction of the carbonyl group.

When *o*-benzoylbenzoic acid was treated with 2.2 equiv of triethylsilane in trifluoroacetic acid at room temperature, 3-phenylphthalide (III) was produced quantitatively. Further reduction to *o*-benzylbenzoic acid did not occur with longer reaction times. Similarly, 3-benzoylpropanoic acid gave 4-phenylbutyrolactone (IV) in 86% yield and 4-phenylbutyric acid in 14% yield when treated with 2.2 equiv of triethylsilane under similar reaction conditions; when only 1.4 equiv of triethylsilane was used, IV was produced quantitatively. An attempt was made to increase the yield of 4-phenylbutyric acid in the reduction of 3-benzoylpropanoic acid by using 8.0 equiv of triethylsilane; however, results identical with those for the reaction with 2.2 equiv of silane were obtained. Attempts were also made to convert the homologous 4-benzoylbutanoic and 5-benzoylpentanoic acids to the δ- and ε-lactones, respectively, by using only 1 equiv of triethylsilane. For these reactions, reported in Table I, only the methylene product and unreacted starting material were observed; no lactones were formed. Thus, even with substituted benzophenones and acetophenones, which were observed in earlier



III



IV

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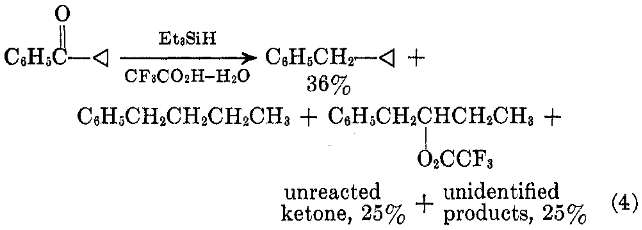
[12] D. N. Kursanov, Z. N. Parnes, N. M. Loim, and G. V. Bakalova, *Dokl. Akad. Nauk SSSR*, **179**, 1106 (1968).

[13] We were not able to determine the amount of *p*-xylene produced directly from the ether under these reaction conditions.

examples to undergo rapid reduction to arylhydrocarbons, a highly specific intramolecular formation of γ-lactones successfully competes with silane reduction to methylene products; the formation of δ- and ϵ-lactone is not competitive with hydride transfer from triethylsilane.

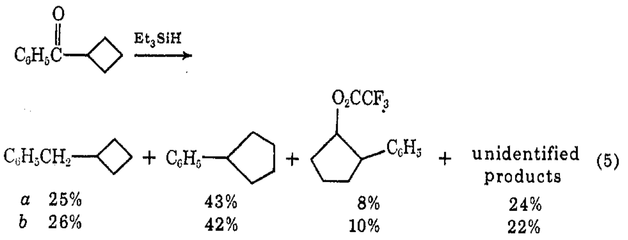
Carbonyl compounds that yielded products that were sensitive to the acidity of the medium were also examined. Phenyl cyclopropyl ketone gave phenylcyclopropylmethane, 1-phenylbutane, and 1-phenyl-2-butyl trifluoroacetate when treated with triethylsilane in aqueous trifluoroacetic acid (eq 4). A number of minor reaction products, each formed in less than 5% yield, were also observed but not identified in this study. When the reduction of phenyl cyclopropyl ketone was performed in trifluoroacetic acid without water, 27% of phenylcyclopropylmethane and 43% of 1-phenyl-2-butyl trifluoroacetate were obtained. The use of carbon tetrachloride as a cosolvent did not increase the yield of phenylcyclopropylmethane. Under the reaction conditions employed phenyl cyclopropyl ketone is stable to trifluoroacetic acid, but phenylcyclopropylmethane reacts with trifluoroacetic acid to form 1-phenyl-2-butyl trifluoroacetate.



$$C_6H_5\overset{O}{\overset{\|}{C}}\text{—}\triangleleft \xrightarrow[CF_3CO_2H\text{–}H_2O]{Et_3SiH} \underset{36\%}{C_6H_5CH_2\text{—}\triangleleft} + C_6H_5CH_2CH_2CH_2CH_3 + C_6H_5CH_2\underset{O_2CCF_3}{\underset{|}{C}}HCH_2CH_3 + \underset{\text{ketone, 25\%}}{\text{unreacted}} + \underset{\text{products, 25\%}}{\text{unidentified}} \quad (4)$$

Carey and Tremper have reported that when cyclopropylphenylcarbinol was treated with trifluoroacetic acid in methylene chloride only *trans*-4-phenyl-3-butenyl trifluoroacetate was formed, and that when the same reaction was performed in the presence of triethylsilane at −15° only a trace amount of the trifluoroacetate and greater than 99% of phenylcyclopropylmethane were produced.[14] We attempted to reduce phenyl cyclopropyl ketone under these same conditions but found that no reduction had occurred, even after 70 hr. Under the reaction conditions reported in Table I neither 4-phenyl-3-butenyl trifluoroacetete nor products derived from trifluoroacetic acid addition to or silane reduction of this olefin were observed.

The reduction of phenyl cyclobutyl ketone by triethylsilane was significantly more rapid than the corresponding reduction of phenyl cyclopropyl ketone. Phenylcyclobutylmethane, phenylcyclopentane, and 2-phenylcyclopentyl trifluoroacetate were formed when phenyl cyclobutyl ketone was treated with triethylsilane in aqueous trifluoroacetic acid or in carbon tetrachloride–trifluoroacetic acid media (eq 5). Nearly identical results were observed despite the differences in the reaction media and the number of equivalents of silane used (see Table I). Neither 1-phenylpentane nor 1-phenyl-2-pentyl trifluoroacetate, the expected product from ring opening of phenylcyclobutylmethane in these reactions, were detected. Phenyl cyclobutyl ketone was stable under the reaction conditions.



[a] Yield in CF_3CO_2H-H_2O. [b] Yield in CF_3CO_2H-CCl_4.

Numerous attempts were made to reduce benzaldehyde to toluene. Under reaction conditions that were successful in reducing *p*-tolualdehyde to *p*-xylene and Friedel–Crafts products, only benzyl trifluoroacetate and dibenzyl ether were produced from benzaldehyde. The use of stronger acids than trifluoroacetic acid (H_2SO_4, HCl, FSO_3H, and FSO_3H–SbF_5 in acetonitrile), longer reaction times, or higher temperatures did not effect the production of toluene. Similarly, *p*-chlorobenzaldehyde, *p*-nitrobenzaldehyde, *p*-cyanoacetophenone, *p*-nitroacetophenone, 1- and 2-naphthaldehydes, and 9-anthraldehyde were reduced to their corresponding trifluoroacetates and symmetrical ethers, but not to the arylhydrocarbon products. Although initial reduction of the carbonyl group proceeded rapidly under the reaction conditions employed, further reduction of trifluoroacetate and ether products was dramatically dependent on substituent effects.

Silane reductions are remarkably selective for the carbonyl group. Other functional groups, which included carboxylate, cyano, and nitro, were not affected during reductions of the carbonyl group. Additionally, displacement of bromide did not occur during the reduction of α-bromoacetophenone.

With respect to physical properties trialkylsilanes and their oxidized products, trialkylsilanols and derivatives of trialkylsilanols, are analogous to their carbon counterparts.[15] In the absence of acid or base functional groups, similarities in polarity render separation of carbon products from silicon products by conventional means of extraction difficult at best. On a small scale, preparative glpc is easily accomplished. On a larger scale, however, alternate means of isolation that cleanly and efficiently separate silane products from carbon products must be employed.

The products from silane reductions of carbonyl compounds in trifluoroacetic acid were the silyl trifluoroacetate and disiloxane (eq 1). After extraction of the reaction mixture with aqueous base the silane products consisted of silanol and disiloxane. When the boiling point of the carbon product was higher than those of the silane products, direct distillation was possible even without basic extraction. However, for arenes with boiling points comparable to those of the silanol or trifluoroacetate, alternate methods, employing the conversion of the silanol to the higher boiling disiloxane, were used. Since trialkylsilanols are readily converted to hexaalkyldisiloxanes under

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[14] F. A. Carey and H. S. Tremper, *J. Amer. Chem. Soc.*, **91**, 2967 (1969).

[15] (a) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960; (b) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965.

basic conditions,[16] simple distillation methods can be used to separate the reduced product from the unreacted trialkylsilane and the disiloxane. Representative examples of reductions that have employed these isolation methods are given in Table III. Generally, the silane reducing agent which yielded a disiloxane having a boiling point sufficiently different from that of the arene provided the best results. Triethylsilane was suitable for carbonyl compounds whose reduced products had a boiling point greater than 300°, tri-*n*-hexylsilane was suitable for the isolation of arylhydrocarbons with boiling point less than 220°, and tri-*n*-propylsilane was found to be suitable for compounds in the intermediate boiling point range.

TABLE III

ISOLATED YIELDS FROM SILANE REDUCTIONS OF ARYLCARBONYL COMPOUNDS IN TRIFLUOROACETIC ACID MEDIA[a]

Carbonyl compd (mmol)	R_3SiH (mmol)	Mmol CF_3CO_2H	Isolation method[b]	Isolated yield, %[c]
p-Benzoylbenzoic acid (6.6)	Et_3SiH (26)	68[d]	Ia	96
4-Benzoylbutanoic acid (16)	Et_3SiH (35)	101	Ia	59
5-Benzoylpentanoic acid (4.8)	Et_3SiH (12)	34	Ia	77
o-Benzoylbenzoic acid (10)	Et_3SiH (14)	121	Ib	74
3-Benzoylpropanoic acid (10)	Et_3SiH (14)	68	Ib	73
1,4-Dibenzoylbutane (5.0)	Et_3SiH (20.0)	34	Ic	72
1,4-Dibenzoylbutane (15)	Et_3SiH (66)	135	Ic	79
4-Nitrobenzophenone (5.0)	Et_3SiH (12)	34	Ic	96
Acetophenone (27)	*n*-Hex_3SiH (60)	135	IIa	65[e]
Acetophenone (20)	*n*-Hex_3SiH (50)	68	IIb	64[f]
Acetophenone (40)	*n*-HexSiH (90)	155	IIc	55[f]
α-Tetralone (25)	Et_3SiH (55)	125	IIb	71[g]
α-Tetralone (25)	Et_3SiH (55)	75[h]	IIb	83[g]
1,3,5-Triacetylbenzene (15)	*n*-Pr_3SiH (90)	180	IIb	54[i]
1,3,5-Triacetylbenzene (15)	*n*-Pr_3SiH (90)	180	IIc	41[j]

[a] See footnote *a*, Table I. Reaction times were at least as long as those reported in Table I. [b] Full procedures are given in the Experimental Section: Ia, products isolated by crystallization or distillation following base extraction and reacidification of extract; Ib, lactone products isolated by crystallization or distillation following extraction; Ic, direct distillation of reaction mixture without extraction; IIa, reaction mixture neutralized with excess Na_2CO_3, KOH, or NaOH and product steam distilled; IIb, distillation from KOH following extraction; IIc, direct distillation of reaction mixture following neutralization with excess Na_2CO_3. [c] Recovery yield of arylhydrocarbon product after recrystallization or fractional distillation. [d] Cosolvent, carbon tetrachloride (7.5 ml), was used. [e] Contains 1 mol % silanol or disiloxane. [f] Less than 5 mol % silicon impurities. [g] After first distillation 25 mol % of hexaethyldisiloxane was present; a second distillation gave tetrahydronaphthalene with 4 mol % disiloxane. [h] Cosolvent, carbon tetrachloride (12.5 ml), was used. [i] Contains 8 mol % disiloxane. [j] Contains 75 mol % disiloxane.

Discussion

Trialkylsilanes are remarkably selective reducing agents. With carbonyl compounds containing carboxylate, cyano, or nitro functional groups, among others, only the carbonyl group is reduced in trifluoroacetic acid media. However, silane reductions of the carbonyl group to methylene are specific for arylcarbonyl compounds and further limited by substituent effects. Only benzaldehydes substituted with activating groups are reduced to arylhydrocarbons, and substitution with one or more strongly activating groups, such as hydroxy, results in predominant Friedel-Crafts alkylation. Reductions of the carbonyl group of aryl ketones to methylene are not so limited, however, as can be seen by the summary given in Table IV.

TABLE IV

SILANE REDUCTIONS OF SUBSTITUTED BENZALDEHYDES, ACETOPHENONES, AND BENZOPHENONES IN TRIFLUOROACETIC ACID MEDIA

	Yield of $ArCH_2R$, %[a]		
Ar	R = H	R = CH_3	R = C_6H_5
p-$CH_3OC_6H_4$	83		
p-$CH_3C_6H_4$	66		
C_6H_5	0	100	100
p-ClC_6H_4	0	100	
p-$HO_2CC_6H_4$			100
p-NCC_6H_4		0	
p-$O_2NC_6H_4$	0	0	100

[a] All compounds investigated were reduced in their corresponding alcohol derivatives, trifluoroacetate and symmetrical ether.

The reduction of the carbonyl group to methylene by trialkylsilanes may be viewed as occurring in two steps: reduction of the carbonyl group to an alcohol or alcohol derivative (eq 6) followed by reduction of

$$R_2C{=}O + R'_3SiH + CF_3CO_2H \longrightarrow R_2CHOH + R'_3SiO_2CCF_3 \\ \text{or } R_2CHO_2CCF_3 \text{ and } (R_2CH)_2O \quad (6)$$

the intermediate alcohol or alcohol derivative (eq 7).

$$R_2CHOH + R'_3SiH + CF_3CO_2H \longrightarrow \\ R_2CH_2 + R'_3SiO_2CCF_3 + H_2O \quad (7)$$

All compounds examined underwent reduction of the carbonyl group; however, of those compounds that were further reduced, only with *p*-tolualdehyde were we able to detect intermediate products.[17] The rate for eq 6 was not drastically affected by structural effects. However, the rate for eq 7 is primarily determined by structural effects and is the principal limiting factor in the use of silanes to convert the carbonyl group to methylene.

Carey and coworkers have studied the process given in eq 7 extensively and have shown that only those alcohols that form relatively stable carbenium ions are reduced to the corresponding alkanes.[10] The formation of arenes in silane reductions of the carbonyl group are similarly limited. Stronger acids than trifluoroacetic acid, which might be expected to provide higher concentrations of carbenium ions, react with trialkylsilanes.

Results from the reduction of phenyl cyclopropyl ketone are consistent with the formation and rapid reduction of phenylcyclopropylcarbinol or its deriva-

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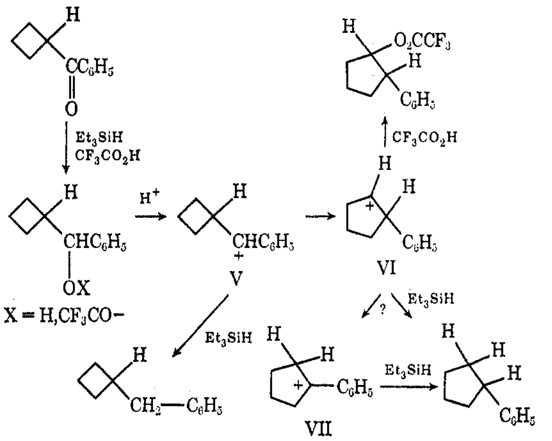
[16] D. N. Kursanov, A. N. Parnes, G. I. Bassova, N. M. Loim, and V. I. Zdanovich, *Tetrahedron*, **23**, 2235 (1967). In attempts to distill reaction products from powdered potassium hydroxide, conditions under which silanol products are converted to potassium silanolates,[15b] disiloxane products often codistilled with the arene products.

[17] However, when triethylsilane was slowly added to acetophenone in trifluoroacetic acid, approximately 2% of the symmetrical ether could be observed after 15 min.

tives. Although at least five minor products are produced in these reductions, the absence of products from ring opening of phenylcyclopropylcarbinol[14] suggests that this reaction is suppressed even at room temperature when phenyl cyclopropyl ketone is reduced by triethylsilane in trifluoroacetic acid media. Ring opening of phenylcyclopropylmethane, however, occurred under all reaction conditions used at a rate comparable to the rate of reduction. The behavior of cyclopropane hydrocarbons in the presence of trifluoroacetic acid and triethylsilane has been studied by Kursanov and coworkers;[18] ring opening occurred in all of the cases studied by these workers.

Triethylsilane was not effective in eliminating ring expansion of phenylcyclobutylcarbinol or its derivatives in trifluoroacetic acid. Only 25% of phenylcyclobutylmethane and more than 50% of ring-expanded products were obtained. These results, which were surprisingly insensitive to the different reaction conditions used, can be explained by the reaction sequence given in Scheme I. The formation of 2-phenylcyclopentyl trifluoroacetate suggests that ring expansion of V is not concurrent with a 1,2-hydride shift to form the more stable tertiary benzylic cation, VII. Although VI may react directly with triethylsilane an alternate process, involving either a 1,2-hydride shift or an elimination–addition sequence and followed by hydride transfer from triethylsilane, can also explain the observed formation of phenylcyclopentane. If triethylsilane does react directly with VI, however, the usefulness of silanes as hydride transfer reagents in studies of carbenium ion processes would be considerably expanded.

SCHEME I



The selectivity, lack of competing reactions with aryl alkyl ketones and diaryl ketones, and short reaction times at room temperature make trialkylsilane reductions a useful method for the conversion of the carbonyl group to methylene. The Clemmensen reduction of these same compounds usually gives coupling products and requires significantly longer reaction times.[19] Although silane products cannot be removed by conventional extractions, simple distillation techniques are adaquate for the isolation of arene products in good yields. Those same compounds that can be formed by Friedel–Crafts acylation can be reduced by trialkylsilanes in trifluoroacetic acid media; the combination of these two methods represents a convenient procedure for the production of arenes by a net Friedel–Crafts alkylation without rearrangement.

Experimental Section

General.—Instrumentation has been previously described.[20] Mass spectra were obtained using a Finnigan Model 1015 gas chromatograph–mass spectrometer operated at 70 eV. Use was made of 5-ft columns of 10% Carbowax 20M, 20% SE-30, 10% SE-30 and a 6-ft column of OV-17, all on Chromosorb P. Triethylsilanol and hexaethyldisiloxane were prepared by conventional methods.[11,21] *o*-Benzoylbenzoic acid and 3-benzoylpropanoic acid were prepared by standard Friedel–Crafts acylation procedures from benzene and phthalic or succinic anhydride. Other carbonyl compounds and all silanes were commercially available and used without further purification. Melting points and boiling points were uncorrected.

General Reduction Procedure.—To a stirred solution of the carbonyl compound (usually 5.0 mmol) in trifluoroacetic acid (usually 20–75 mmol, 4–15 equiv) or in trifluoroacetic acid–cosolvent mixture at room temperature was added the trialkylsilane (usually 11 mmol, 2.2 equiv). With the exception of reactions in trifluoroacetic acid–nitromethane or aqueous acid, or those using tri-*n*-hexylsilane, all solutions were homogeneous. Rapid addition of trialkylsilane to the trifluoroacetic acid solution produced a noticeable exothermic reaction; dropwise addition of the silane or use of a cosolvent moderated the temperature increase. Reactions proceeded faster at higher temperatures; triethylsilane reacted slowly with trifluoroacetic acid and at 50–60° was stable for a period of days. The progress of each reaction was monitored by pmr spectroscopy. Products were identified from their chemical shifts and the multiplicity of their pmr absorptions. Yields were based on integrations of the individual and characteristic absorption signals of each compound through reference to the total phenyl absorption and/or an added internal standard. Integrations were maximized and averaged over several integrations of the same signal. Reproducibility was shown to be ±2% in duplicate runs.

The products from several reactions listed in Table I were further analyzed following work-up. Usually water or a saturated sodium bicarbonate solution was added to the trifluoroacetic acid reaction solution followed by ether, the ether layer was separated, and the aqueous layer was washed with ether. The combined ether solution was dried over anhydrous magnesium sulfate, and the ether was removed under reduced pressure. The products from the reduction of *p*-anisaldehyde by triethylsilane were subjected to glpc analysis; triethylsilanol and hexaethyldisiloxane were identified by comparison of glpc retention times to those of authentic samples and peak enhancement. *p*-Methylanisole was collected and identified by pmr spectroscopy. Isodurene was isolated after work-up by distillation of the reaction products from the reduction of 2,4,6-trimethylbenzaldehyde and identified by pmr spectroscopy through comparison to an authentic sample. Dibenzyl ether and benzyl trifluoroacetate were also identified after work-up by glpc comparison to authentic samples.

Friedel–Crafts alkylation products were inferred from the pmr spectra of some of the reaction mixtures. In reductions of *p*-tolualdehyde absorptions were observed at δ 3.7–3.9 which were similar to those found when *p*-methylbenzyl alcohol was treated with trifluoroacetic acid without added trialkylsilane. Similarly, absorptions in the same region, attributable to a methylene group adjacent to two aromatic rings, were observed in reductions of *p*-anisaldehyde, 2,4,6-trimethylbenzaldehyde, vanillin, and salicylaldehyde.

Reduction of 1,4-Dibenzoylbutane by Triethylsilane. Identification of Silane Products.—To a stirred solution of 1,4-dibenzoylbutane (4.00 g, 15.0 mmol) and triethylsilane (7.65 g, 66.0 mmol) was added 10.0 ml (135 mmol) of trifluoroacetic acid dropwise over a 1-hr period; during the addition of the last 5.0

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[18] Z. N. Parnes, G. A. Khotimskayu, R. V. Kudryavtsev, M. Yu Lukina, and D. N. Kursanov, *Dokl. Akad. Nauk SSSR*, **184**, 615 (1969).

[19] H. L. Bradlow and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **69**, 1254 (1947); W. P. Duncan, J. E. Russell, E. J. Eisenbraun, G. W. Keen, P. W. Flanagan, and M. C. Hamming, *J. Org. Chem.*, **37**, 142 (1972).

[20] M. P. Doyle and W. Wierenga, *J. Amer. Chem. Soc.*, **94**, 3896 (1972).

[21] L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Amer. Chem. Soc.*, **68**, 2282 (1946).

ml of acid, the reaction mixture was cooled in an ice bath. After 19 hr pmr analysis indicated complete reduction, and the reaction solution was directly distilled through a short-path distillation apparatus. Four fractions were collected: bp 25–52° (17 Torr), triethylsilyl trifluoroacetate (2.51 g, 11.6 mmol), and trifluoroacetic acid; bp 52–54° (17 Torr), triethylsilyl trifluoroacetate (3.17 g, 14.7 mmol); bp 120–160° (17 Torr), hexaethyldisiloxane (4.79 g, 19.5 mmol); and bp 107–109° (0.05 Torr), 1,6-diphenylhexane (2.80 g, 11.8 mmol, 78.5%). Hexaethyldisiloxane was identified by glpc comparison to an authentic sample. Triethylsilyl trifluoroacetate was isolated by glpc and characterized from its ir spectrum (carbonyl absorption at 1765 cm^{-1}) and its pmr spectrum; the pmr spectrum of the isolated product was identical with that of a sample prepared by treating triethylsilanol with trifluoroacetic acid. The pmr spectrum and boiling point (lit.[22] bp 206–208°) of 1,6-diphenylhexane were consistent with its structure. The total yield of recovered silane products was 99%.

Triethylsilane Reduction of Phenyl Cyclopropyl Ketone.—Reactions were performed according to the general procedure. The products after working were subjected to glpc analysis. In addition to triethylsilanol and hexaethyldisiloxane, nine peaks were observed using a 10% Carbowax 20M column. The major products, phenylcyclopropylmethane, 1-phenylbutane, 1-phenyl-2-butyl trifluoroacetate, and phenyl cyclopropyl ketone, were identified by retention times and peak enhancement using authentic samples. 1-Phenyl-2-butyl trifluoroacetate was prepared by the reaction of phenylcyclopropylmethane with trifluoroacetic acid. Yields were calculated by determining the peak areas of each compound relative to that of phenyl cyclopropyl ketone and using the relative response ratio of each product. Yields determined by glpc analysis were within 2% of those calculated by pmr analysis using an internal standard. Pmr analysis of the reaction products in the δ 3.8–7.0 region shows only a single quintet centered at δ 5.20, attributable to 1-phenyl-2-butyl trifluoroacetate.

Triethylsilane Reduction of Phenyl Cyclobutyl Ketone.—Reactions were performed according to the general procedure. The products after work-up were subjected to glpc analysis. In addition to hexaethyldisiloxane, five peaks were observed using a 10% Carbowax 20M column. The three major products were isolated by glpc. Phenylcyclopentane was identified from its pmr spectrum and by glpc retention time and peak enhancement using an authentic sample. Phenylcyclobutylmethane was identified from its pmr and mass spectra: pmr (CCl_4) δ 7.15 (s, 5 H), 2.67 (broadened singlet, 2 H), and 2.3–1.5 (multiplet, 7 H); mass spectrum *m/e* (relative intensity) 146 (11, parent ion), 118 (83), 117 (99), 114 (50), 91 (100). The structure of 2-phenylcyclopentyl trifluoroacetate was inferred from spectral data: ir (CCl_4) carbonyl absorption at 1780 and strong absorptions at 1160 and 1220 cm^{-1}; pmr (CCl_4) δ 7.25 (s, 5 H), 5.31 (multiplet, 1 H), 3.32 (multiplet, 1 H), 2.6–1.6 (multiplet, 6 H); mass spectrum[23] *m/e* (rel intensity) 145 (20, M − CF_3CO_2), 144 (62, M − CF_3CO_2H), 143 (36), 129 (51), 117 (44), 115 (31), 91 (100). Yields were determined by pmr analysis using an internal standard. Pmr analysis of the reaction products in the δ 3.9–7.0 region shows only the multiplet centered at δ 5.31, attributable to 2-phenylcyclopentyl trifluoroacetate.

Isolation of 6-Phenylhexanoic Acid. Method Ia.—Triethylsilane (1.35 g, 11.6 mmol) was added to 5-benzoylhexanoic acid (1.00 g, 4.85 mmol) in 2.5 ml of trifluoroacetic acid according to the general procedure. After 3 days at room temperature, a 5% solution of sodium hydroxide was added until the reaction mixture was basic to litmus. The aqueous layer was washed once with ether and acidified with hydrochloric acid. The acidic solution was washed twice with 30-ml portions of ether, the combined ether solution was dried over anhydrous sodium sulfate, and the ether was removed under reduced pressure. The resulting residue was distilled at 37 Torr to give 0.71 g (3.70 mmol, 77% yield) of 6-phenylhexanoic acid, bp 218–219° (lit.[24] bp 180–90° at 17 Torr).

Isolation of 4-Phenyl-4-Hydroxybutyric Acid γ-Lactone (IV). Method Ib.—3-Benzoylpropanoic acid (1.78 g, 10.0 mmol) was added to triethylsilane (1.62 g, 14.0 mmol) in 5.0 ml of trifluoroacetic acid. After 4 hr at room temperature the reaction solution was neutralized by adding a saturated solution of sodium bicarbonate. The resulting solution was washed three times with ether, the combined ether extracts were dried with anhydrous sodium sulfate, and the ether was removed under reduced pressure. The resulting residue was a two-phase liquid; the lower layer (1.69 g) consisted of IV (91%) and triethylsilanol. The lower layer was a viscous oil that after crystallization and washing with heptane gave 1.20 g (7.32 mmol, 73% yield) of IV, mp 34.0–35.0° (lit.[25] mp 36–37°).

Isolation of *p*-Nitrodiphenylmethane. Method Ic.—*p*-Nitrobenzophenone (1.14 g, 5.0 mmol) was added to triethylsilane (1.40 g, 12.0 mmol) followed by 2.5 ml of trifluoroacetic acid. After 47 hr at room temperature the reaction mixture was directly distilled under reduced pressure to give 1.03 g (4.8 mmol, 96% yield) of *p*-nitrodiphenylmethane, bp 114–115° (0.05 Torr) [lit.[26] bp 178–181° (4 Torr)].

Isolation of Ethylbenzene. Method II. A.—Acetophenone (3.26 g, 27.2 mmol) was added to tri-*n*-hexylsilane (17.00 g, 59.7 mmol) followed by 10 ml of trifluoroacetic acid. After 15 hr at room temperature 85% aqueous potassium hydroxide (10 g, 0.18 mol) was added to the reaction mixture and the resulting solution was steam distilled. The distillate was cooled and the organic layer was separated from the aqueous layer. The organic layer contained 1.86 g (17.6 mmol, 65% yield) of ethylbenzene that showed only a trace of contaminant by pmr analysis.

B.—The reaction mixture, following extraction to remove trifluoroacetic acid, was distilled from solid powdered potassium hydroxide. Ethylbenzene distillation required pot temperatures in excess of 200°. Although a significant amount of the arene was retained in the residue following distillation, a 64% yield of ethylbenzene was recovered.

C.—The reaction mixture was treated with excess sodium carbonate (0.10 mol) and the resulting solution distilled. Throughout the distillation foaming occurred, and water codistilled with ethylbenzene. The distillate was taken up in ether, dried over anhydrous sodium sulfate, and distilled to give a 55% yield of ethylbenzene that contained a small amount of silane impurity. Inspection of the pot residue from the initial distillation showed substantial amounts of ethylbenzene and silane products.

Registry No.—Trifluoroacetic acid, 76-05-1; triethylsilane, 617-86-7; triethylsilyl trifluoroacetate, 562-98-1; hexaethyldisiloxane, 994-49-0; 1,6-diphenylhexane, 1087-49-6; phenylcyclobutylmethane, 5244-88-2; 2-phenylcyclopentyl trifluoroacetate, 40127-82-0; 6-phenylhexanoic acid, 5581-75-9; 5-benzoylhexanoic acid, 40127-84-2; 4-phenyl-4-hydroxybutyric acid γ-lactone, 1008-76-0; 3-benzoylpropanoic acid, 2051-95-8; *p*-nitrophenylmethane, 1817-77-2; ethylbenzene, 100-41-4; tri-*n*-hexylsilane, 2929-52-4; *o*-benzoylbenzoic acid, 85-52-9.

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(22) E. A. Evans and M. Whalley, *J. Chem. Soc.*, 3642 (1954).

(23) The parent ion was not observed; the first observed *m/e* value was at 145.

(24) J. V. Braun, *Ber.*, **44**, 2867 (1911).

(25) R. R. Russell and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **69**, 11 (1947).

(26) G. S. Kolosnikov, V. V. Korshak, and T. V. Smirnova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk.*, 1123 (1958); *Chem. Abstr.*, **53**, 3135 (1959).