phenylcarbinol, optical purity 27.2%, was recovered upon hydrolysis.

(19) A control of the residual optically active 2-methylbutyl group bound to the zinc atom on the stereochemistry of the MPV reaction seems to be excluded.[17] In fact, a similar result was obtained when isobutyl[(*S*)-1-phenyl-2,2-dimethylpropoxy]zinc (optical purity 10.2%) was heated at 86.5° for 24 hr with an equivalent amount of *tert*-butyl phenyl ketone; the carbinol recovered was 7.2% optically pure.

(20) See ref 6c and 7a and references cited therein.

Silane Reductions in Acidic Media. III. Reductions of Aldehydes and Ketones to Alcohols and Alcohol Derivatives. General Syntheses of Alcohols, Symmetrical Ethers, Carboxylate Esters, and Acetamides[1a]

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Aldehydes and ketones are reduced by alkylsilanes to alcohols in aqueous acidic media; both concentrated hydrochloric acid and aqueous sulfuric acid are suitable aqueous acids. A nonreactive solvent such as acetonitrile or ethyl ether is required to minimize ether formation. Symmetrical ethers are formed by silane reductions of aldehydes and ketones in anhydrous acidic solutions under conditions where acid-catalyzed alcohol dehydration does not occur. Carboxylate esters and symmetrical ethers are formed by silane reductions of aldehydes and ketones in carboxylic acid media. Low temperatures and a low concentration of carboxylic acid favors the production of symmetrical ether; ester formation is favored in the reductions of ketones and in reductions using carboxylic acids comparable in acid strengths to formic and acetic acids. In acetonitrile using aqueous sulfuric acid silane reductions of ketones and aryl aldehydes yield N-substituted acetamides. The optimum reaction conditions and limitations of these reactions are described. Evidence concerning the mechanism of these interrelated reactions is presented and discussed.

In recent years silanes have received increased interest as reducing agents for organic compounds. Organosilanes are nonpolar liquids or solids, soluble in a wide range of organic solvents, and stable to strong bases and strong acids, except concentrated mineral acids.[2] Like the boron and aluminum hydrides, silicon hydrides are polarized with a greater electron density at hydrogen than at silicon; hydride transfer from silicon to electropositive carbon is thermodynamically favorable.[3] Unlike reductions by the boron and aluminum hydrides which require no external acid catalyst, however, organosilanes require activation of the carbon center by a Lewis acid before hydride transfer can occur.

Few reducing agents are as selective as organosilanes toward the carbonyl group of aldehydes and ketones. We have previously reported that reduction of the carbonyl group of aryl aldehydes and ketones to methylene in trifluoroacetic acid occurs without concurrent reduction of the carboxylic acid, carboxylate ester, cyano, nitro, or bromide functional groups.[1a] Olefins and alcohols are reduced to hydrocarbons in acidic media only if a relatively stable carbenium ion intermediate can be formed.[4] Terminal arylacetylenes are reduced in low yield to the corresponding alkane by triethylsilane in trifluoroacetic acid;[5] however, reaction times are long and acid-catalyzed solvation of the carbon–carbon triple bond may have preceded reduction by the silane.

Excluding photochemical reductions involving silanes,[6] three methods, trichlorosilane–tertiary amine reductions, zinc chloride catalyzed reductions, and reductions in trifluoroacetic acid, have had the widest application for reductions of aldehydes and ketones. Benkeser has used trichlorosilane–tertiary amine combinations to effect reductive silylation of aromatic aldehydes and ketones;[7] this reaction probably involves the trichlorosilyl anion[7b] and is, at present, generally applicable only to nonenolizable carbonyl compounds. With trialkylsilanes, however, reactions catalyzed by zinc chloride and leading to either the corresponding symmetrical ether and alkyl silyl ether with aldehydes or to the alkyl silyl ether with ketones appear to have no such limitation for enolizable carbonyl compounds.[8] Kursanov and coworkers have reported several examples of triethylsilane reductions of aldehydes and ketones in trifluoroacetic acid;[4a,9] aldehydes are reduced to the corresponding symmetrical ethers and trifluoroacetates while ketones are reduced to trifluoroacetate esters. We wish to report that aldehydes and ketones can be selectively reduced by organosilanes to alcohols, carboxylate esters, symmetrical ethers, or acetamides by suitable changes in the reaction media.

Results

Preparation of Alcohols. Although trifluoroacetate esters, formed by silane reduction of aldehydes and ketones in trifluoroacetic acid,[4a,9] and alkyl silyl ethers, formed from aldehydes and ketones by silane reduction with zinc chloride catalysis,[8] are readily hydrolyzed to the corresponding alcohols under relatively mild conditions, these methods offer little advantage over existing reduction methods for the preparation of simple alcohols. In addition, the production of symmetrical ethers from aldehydes in a competitive process further complicates the reduction process. Even though alcohols may be the primary products in these reactions, there has been no report of a direct and general method for the synthesis of alcohols from aldehydes and ketones by silane reduction. We have found, however, that silane reductions can be directed to form alcohols if water is added to the reaction medium (eq 1).

$$R_2C{=}O + R'_3SiH + H_2O \xrightarrow{H^+} R_2CHOH + R'_3SiOH \quad (1)$$

The product composition from the reductions of representative aldehydes and ketones by triethylsilane in aqueous acidic media is given in Table I. (Additional data on benzaldehyde are summarized in supplementary material; see paragraph at end of paper). Triethylsilanol was either

Table I
Triethylsilane Reductions of Aldehydes and Ketones in Aqueous Acidic Media[a]

							Yield, %[d]		
Carbonyl compd (mmol)	Registry no.	Et_3SiH, mmol	Solvent (ml)	Acid[b] (ml)	H_2O, ml	Reaction time,[c] hr	R_2-CH-OH	(R_2-CH)$_2$O	Other[c]
C_6H_5CHO (9.9)	100-52-7	11.2	CH_3CN (5.0)	HCl (1.0)		3.5	88	6	6[f]
C_6H_5CHO (5.0)		5.5	CH_3CO_2H (2.5)	HCl (1.0)		4.0	9	3	88[g]
C_6H_5CHO (5.0)		6.4	CH_3CN (2.5)	H_2SO_4 (1.0)		1.0	0	50	50[h]
C_6H_5CHO (5.1)		6.2	CH_3CN (2.5)	H_2SO_4 (2.0)	1.0	1.25	32	27	41[h]
C_6H_5CHO (5.0)		6.3	CH_3CN (2.5)	H_2SO_4 (1.0)	1.0	1.25	88	12	0
C_6H_5CHO (5.0)		6.3	CH_3CN (2.5)	H_2SO_4 (0.5)	1.0	24	96	4	0
C_6H_5CHO (5.0)		6.4	Sulfolane (2.5)[i]	H_2SO_4 (0.5)	1.0	32	98	2	0
Cyclohexanone (5.0)	108-94-1	5.5	CH_3CN (2.5)	HCl (2.0)		2.5	100	0	0
Cyclohexanone (20.0)		25.1	CH_3CN (10)	H_2SO_4 (4.0)	4.0	1.5	100	0	0
$(CH_3)_2CO$ (5.1)	67-64-1	5.6	CH_3CN (2.5)	HCl (2.0)		2.5	100	0	0
$CH_3(CH_2)_5CHO$ (5.0)	111-71-7	5.6	CH_3CN (2.5)	HCl (2.0)		3.0	100	0	0
$CH_3(CH_2)_5CHO$ (10.1)		12.6	CH_3CN (5.0)	H_2SO_4 (2.0)	2.0	1.25	97	3	0
2-Ethylhexanal (20.1)	123-05-7	25.0	CH_3CN (10)	H_2SO_4 (4.0)	4.0	2.0	90	10	0
$(CH_3)_3CCOCH_3$ (20.0)	75-97-8	25.0	CH_3CN (10)	H_2SO_4 (4.0)	4.0	1.2	100	0	0
$(C_6H_5)_2CO$ (20.0)	119-61-9	50.2	CH_3CN (10)	H_2SO_4 (4.0)	4.0	72	0	0	100[j]

[a] Reactions were run at room temperature (28 ± 3°). Carbonyl compounds, acids, and triethylsilane were commercially available and used without prior purification. Reaction mixtures were heterogeneous. [b] Concentrated hydrochloric acid (37–38% by weight); trifluoroacetic acid (99+%); concentrated sulfuric acid (96.8% by weight). [c] Time at which reaction solution was analyzed; does not necessarily reflect required reaction time. [d] Relative yields of products based on pmr analyses using an internal standard. Greater than 80% recovery of products was obtained. Analyses prior to work-up showed no difference between absolute and relative yields of products. Unless noted otherwise, complete reduction of the carbonyl compound was observed. [e] Product identified by pmr and/or glpc analyses. [f] Approximately equal amounts of benzyl chloride and benzyl acetate. [g] Benzyl acetate. [h] *N*-Benzylacetamide. [i] Reaction solution was homogeneous. [j] 17% diphenylmethane + 83% unreacted benzophenone. Attempted reduction using concentrated hydrochloric acid gave similar results.

the only or the major silane product in these reactions; hexaethyldisiloxane was present in only minor amounts. Both concentrated hydrochloric and aqueous sulfuric acids were satisfactory for alcohol production with a minimum of side reactions. Greater than 1 molar equiv of hydrochloric acid, compared to the carbonyl compound, was used for the reactions described in Table I. When less than 1 molar equiv of hydrochloric acid (0.5 equiv) was used, reduction did occur but was slow; only 30% reduction occurred over a 20-hr period.

Although all mixtures of sulfuric acid and water between 96 and 20% aqueous sulfuric acid (by volume) were sufficiently acidic to effect reduction by triethylsilane, long reaction times were necessary in 20% aqueous sulfuric acid (>48 hr) and the yield of alcohol was low when the ratio of water to sulfuric acid was less than that in 50% aqueous sulfuric acid. The optimum molar ratio of water to sulfuric acid used for reductions of carbonyl compounds to alcohols was between 6.3 and 3.3 (33–50% aqueous sulfuric acid).

An interfacing nonhydroxylic organic solvent is a necessary requirement for the production of alcohols from aldehydes and, to a lesser extent, from ketones. When either benzaldehyde or heptanal was reduced by triethylsilane using 50% aqueous sulfuric acid at room temperature without added organic solvent, the corresponding symmetrical ether was formed as the sole or major product. Cyclohexanone was reduced to cyclohexanol with cyclohexyl ether formed as a minor product when no organic solvent was used. When benzaldehyde was reduced by triethylsilane using concentrated hydrochloric acid, benzyl alcohol was converted to benzyl chloride; the formation of benzyl chloride was minimized when acetonitrile was employed as a reaction solvent.

Acetonitrile and sulfolane were satisfactory as interfacing solvents. However, no reduction of benzaldehyde occurred over a 3-hr period when either benzene or dimethylformamide was used. Although relative product yields were not changed by varying the amount of nonhydroxylic organic solvent with respect to the aqueous acid, reaction times were lengthened as more organic solvent was used. With acetonitrile reaction times were less than 1 hr when the volumes of acetonitrile and aqueous acid were approximately equal; doubling the volume of acetonitrile over that of the aqueous acid increased reaction times to approximately 3 hr. When the hydroxylic solvent, acetic acid, was used in the reduction of benzaldehyde by triethylsilane with hydrochloric acid, benzyl acetate was formed in greater than 80% yield. Aqueous trifluoroacetic acid or an acetonitrile solution of aqueous trifluoroacetic acid led to the production of the trifluoroacetate product as a major competing process.

Benzophenone was reduced at a much slower rate than either benzaldehyde or the aliphatic aldehydes and ketones, and only diphenylmethane was produced. Benzhydrol is apparently reduced at a faster rate than benzophenone.[1a] 9,10-Anthroquinone was not reduced in 50% aqueous sulfuric acid media.

That the acidic conditions used for these reductions are not sufficiently strong to ionize the alcohols produced from aliphatic aldehydes and ketones is shown by the production of 3,3-dimethyl-2-butanol without rearrangement from 3,3-dimethyl-2-butanone using 50% aqueous sulfuric acid (Table I). Similarly, 2-ethyl-1-hexanol did not rearrange under the reaction conditions employed.

We have previously described suitable methods for the isolation of organic reduction products from silane products.[1a] Ketones may be reduced by an alternate procedure using *n*-butylsilane as the reducing agent and ethyl ether as the interfacing solvent. The silane product is a polymeric siloxane from which the alcohol can be conveniently distilled following simple extraction procedures. Using this latter method cyclohexanol was isolated in 56% yield and cyclooctanol in 78% yield following reduction of the respective ketone; analysis prior to work-up showed that the alcohol was the only organic product. Aldehydes are reduced primarily to symmetrical ethers when *n*-butylsilane is used; for example, octanal was reduced to an alcohol–ether mixture from which 1-octanol was isolated in 31% yield and 1-octyl ether in 61% yield. Tetramethyldisiloxane similarly reduced octanal to a mixture of 1-octanol and 1-octyl ether.

Table II
Triethylsilane Reductions of Aldehydes and Ketones in Carboxylic Acid Media[a]

Carbonyl compd (mmol)	Registry no.	Et_3SiH, mmol	R″COOH (mmol)	Solvent (ml)	Reaction time,[b] hr	Yield,[c] %		
						$(R_2CH)_2O$	$R_2CHOOCR$	Other[d]
C_6H_5CHO (20.0)		24	CF_3CO_2H (30)		0.50	87	13	0
C_6H_5CHO (2.5)		2.8	CF_3CO_2H (25)	$CHCl_3$ (2.5)	0.25	93	7	0
C_6H_5CHO (2.5)		2.8	CF_3CO_2H (25)	CCl_4 (2.5)	0.25	89	11	0
C_6H_5CHO (2.5)		2.6	CF_3CO_2H (5.0)	CCl_4 (2.5)	24	49	51	0
C_6H_5CHO (2.5)		2.8	CF_3CO_2H (5.0)	CH_3CN (2.5)	0.25	96	4	0
C_6H_5CHO (2.5)		2.8	Cl_2CHCO_2H (15)		0.5	93	7	0
C_6H_5CHO (2.5)		2.8	HCO_2H (35)		8	12	88	0
C_6H_5CHO (2.5)		2.8	CH_3CO_2H (23)		5	8	27	65[e]
p-$NO_2C_6H_4CHO$ (5.0)	555-16-0	11.0	CF_3CO_2H (55)		5	33	67	0
p-ClC_6H_4CHO (5.0)	104-88-1	11.0	CF_3CO_2H (55)		10	80	20	0
p-$CH_3C_6H_4CHO$ (5.0)	104-87-0	30	CF_3CO_2H (12.5)	CH_2Cl_2 (2.5)	6	81	17	2[f]
					118	70	22	8[f]
p-$NO_2C_6H_5COCH_3$ (5.0)	100-19-6	30	CF_3CO_2H (50)	CCl_4 (2.5)	22	7	93	0
1-Naphthaldehyde (5.0)	66-77-3	30	CF_3CO_2H (12)		1.5[h]	67	33	0
2-Naphthaldehyde (5.0)	66-99-9	30	CF_3CO_2H (12)		18	84	16	0
$C_6H_5COCH_2Br$ (2.5)	70-11-1	6.3	CF_3CO_2H (50)		0.25	5	80	15[g]
					44	0	12	88[g]
$(CH_3)_2CO$ (5.0)		5.5	CF_3CO_2H (100)		1.3	32	68	0
Cyclohexanone (5.0)		5.5	CF_3CO_2H (100)		1.5	25	75	0
Cyclohexanone (1.0)		1.0	CF_3CO_2H (3.0)		1.0	42	58	0
$CH_3(CH_2)_5CHO$ (5.0)		5.5	CF_3CO_2H (100)		0.75	90	10	0
$CH_3(CH_2)_{10}CHO$ (20)	112-54-9	20	CF_3CO_2H (50)		16[h]	93	7	0

[a] Reactions were run at room temperature (28 ± 3°) unless specified otherwise. Reaction solutions were homogeneous. [b] Time at which reaction solution was analyzed; does not necessarily reflect required reaction time. [c] Relative yields of products based on pmr analyses using an internal standard. [d] Product identified by pmr and/or glpc analyses. [e] Unreacted benzaldehyde. [f] p-Xylene and small amount of Friedel–Crafts alkylation product. [g] β-Phenylethyl bromide. [h] Reaction run at 0°.

Reductions by n-butylsilane in aqueous acidic media require 0.33 mol of silane per mole of carbonyl compound. In aqueous acidic media initial hydride transfer from n-butylsilane is slow compared to subsequent hydride transfer reactions from soluble silane compounds. An equivalent excess of n-butylsilane was usually added, however, because insoluble polymeric hydrosiloxane formed during the reaction, noticeably decreasing the rate of further reduction of aldehydes or ketones, and because n-butylsilane slowly hydrolyzed in the aqueous sulfuric acid media.

Formation of Symmetrical Ethers and Carboxylate Esters. When aldehydes or ketones are reduced in acidic media, symmetrical ethers are formed in competition with the desired product.[4a,8,9] In reactions in which a carboxylic acid is used both the unsymmetrical ether and carboxylate ester are produced (eq 2). Table II describes the results

$$R_2C{=}O + R'_3SiH + R''COOH \longrightarrow R_2CHOCHR_2 + R_2CHOOCR'' + R'_3SiOOCR'' + R_3'SiOSiR_3' \quad (2)$$

from the reductions of aldehydes and ketones by triethylsilane in carboxylic acid media. Ethers are not formed from alcohols under the reaction conditions reported in Table II. The relative yield of symmetrical ether is greater in the reductions of aldehydes than in the reductions of ketones under similar reaction conditions. For example, heptanal yields 90% of 1-heptyl ether and 10% of 1-heptyl trifluoroacetate, whereas cyclohexanone gave 75% of cyclohexyl trifluoroacetate and only 25% of cyclohexyl ether when triethylsilane reductions were performed in trifluoroacetic acid.

In the reductions of para-substituted benzaldehydes in trifluoroacetic acid media the relative yield of the symmetrical ether increased with the electron-donating ability of the substituent in the order p-NO_2 (32%) < p-Cl (80%) < H (89%). Under the reaction conditions employed the ether and trifluoroacetate were not interconverted. With aryl aldehydes having para-substituted electron-donating groups such as methyl, however, the symmetrical ether was converted to the trifluoroacetate, and the trifluoroacetate was reduced to the corresponding hydrocarbon.[1a]

Acids whose acidity constants are greater than that of acetic acid can be used as solvents as well as the proton source in the reductions of carbonyl compounds by triethylsilane at room temperature. Acetic acid is effective in causing reduction only at steam bath temperatures; no reduction occurred over a 12-hr period in acetic acid at room temperature. Increasing the basicity of the carboxylic acid also increases the relative proportion of carboxylate ester to symmetrical ether; whereas only 19% benzyl trifluoroacetate is produced in the reduction of benzaldehyde in trifluoroacetic acid, 88% benzyl formate formed in the corresponding reduction in 97% formic acid. With trifluoroacetic and stronger acids the acid need not be used as the solvent; reductions occurred in carbon tetrachloride or acetonitrile using 1–2 equiv of trifluoroacetic or p-toluenesulfonic acids. Reduction of benzaldehyde (2.5 mmol) by triethylsilane (2.8 mmol) using 1 equiv of p-toluenesulfonic acid in acetonitrile (2.5 ml) gave benzyl ether (70%), benzyl alcohol (18%), and benzyl p-toluenesulfonate (12%). Both reaction times and the relative yields of symmetrical ether are, however, dependent on the amount of acid present.

In the reduction of benzaldehyde by triethylsilane in dilute trifluoroacetic acid the symmetrical ether is formed as the sole or major product during the first half-life; benzyl trifluoroacetate is produced later in the reduction (Figure 1). Benzyl alcohol and benzyl triethylsilyl ether are present during the reaction and the sum of their yields remains constant throughout the second half-life. Under the reaction conditions employed benzyl ether is not formed from benzyl alcohol, benzyl trifluoroacetate, or benzyl triethylsilyl ether. Nearly identical results were obtained when tri-n-hexylsilane was used as the reducing agent.

As shown by the data in Table II, symmetrical ethers of aldehydes can be conveniently prepared in good yields by triethylsilane reductions in trifluoroacetic acid media. With the exception of the p-nitrobenzaldehyde, aryl aldehydes form symmetrical ethers in greater than 80% yield.

Table III
Reductions of Cyclohexanone in Trifluoroacetic Acid[a]

Temp, C°	Cyclohexanone, mmol	n-$BuSiH_3$, mmol	CF_3CO_2H, mmol	Reaction time,[b] hr	Yield,[c] % Ether	Yield,[c] % Trifluoroacetate
55	2.0	1.0	12.0	3.5	38	62
55	2.0	1.0	5.0	1.5	47	53
25	1.0	0.5	3.0	24	49	51
0	2.0	1.0	12.0	3.5	60	40
0	2.0	1.0	6.0	24	67	33
−15	30	15	90	25	82	18
−15[d]	40	20	100	72	90	10

[a] Reaction solutions were homogeneous. [b] See footnote *b*, Table II. [c] See footnote *c*, Table II. [d] Acid added slowly over a 1-hr period. Cyclohexyl ether was isolated in 80% yield.

Table IV
Triethylsilane Reductions of Aldehydes and Ketones in Acetonitrile Mixtures with Aqueous Sulfuric Acid[a]

Carbonyl compd	Registry no.	Reaction time, hr	Amide product	Relative yield, %[b]	Isolated yield, %[c]
Benzophenone		48	*N*-(Diphenylmethyl)-acetamide	85[d]	63
Acetophenone	98-86-2	72	*N*-(1-Phenylethyl)-acetamide	100	85[e]
Benzaldehyde		74	*N*-Benzylacetamide	89[f]	80
Cyclohexanone		72	*N*-Cyclohexylacetamide	50[g]	30
Norcamphor	497-38-1	65	*N*-(*exo*-Bicyclo[2.2.1]hept-2-yl)acetamide	90[h]	78
Octanal	124-13-0	72		0[i]	

[a] Reactions were run at room temperature (28 ± 3°) using 60 mmol of the aldehyde or ketone, 66 mmol of triethylsilane, 9.0 ml of concentrated sulfuric acid, 3.0 ml of water, and 15 ml of acetonitrile. [b] Of the amide product. [c] Of the purified amide product after recrystallization. [d] 15% diphenylmethane. [e] Average of two reactions. [f] 11% benzyl ether. [g] 50% of a mixture of cyclohexyl ether and cyclohexanol. [h] 10% of the symmetical ether was detected. [i] Only 1-octanol and 1-octyl ether were observed.

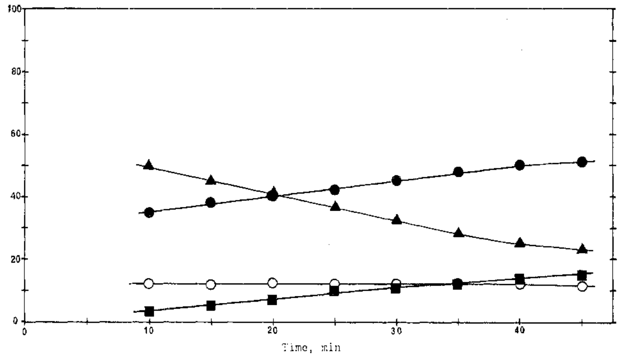


Figure 1. Relative percentages of benzaldehyde (▲), benzyl ether (●), benzyl trifluoroacetate (■), and the sum of benzyl alcohol and benzyl triethylsilyl ether (○) *vs.* time from the reduction of benzaldehyde by triethylsilane in carbon tetrachloride containing trifluoroacetic acid (2 equiv).

p-Toluyl ether was formed in 91% yield when *p*-tolualdehyde (5.0 mmol) was reduced at room temperature by triethylsilane in acetonitrile (2.5 ml) using a small amount of concentrated sulfuric acid (0.25 molar equiv); competitive production of *p*-xylene[1a] was minimized under these conditions. Symmetrical ethers of aldehydes were isolated by conventional methods: 2-naphthyl ether was isolated in 80% yield by crystallization, and benzyl ether (88%), *n*-heptyl ether (70%), and *n*-dodecyl ether (82%) were distilled from silane products.

Silane reductions of ketones do not favor the formation of symmetrical ethers under reaction conditions where aldehydes yield predominantly ether products. Previous reports of silane reductions of ketones indicate an overwhelming preference for trifluoroacetate derivatives when the reductions are performed in trifluoroacetic acid,[4a,9] or for alkyl silyl ethers when Lewis acid catalysts are used.[8] We have found, however, that reduction of cyclohexanone by *n*-butylsilane in trifluoroacetic acid at −15° produces cyclohexyl ether as the predominant product. The effects of changes in temperature, silane, and the amount of trifluoroacetic acid on the relative yields of products from cyclohexanone reductions are given in Table III. Concentrated sulfuric acid, even when only 1 molar equiv was used, hydrolyzed the silane and gave complex mixtures of products. In addition to the preference for ether production when *n*-butylsilane is used, this silane forms a polymeric siloxane from which the ether is conveniently separated. Cyclohexyl ether was isolated in 80% yield from the reduction of cyclohexanone by *n*-butylsilane at −15°.

When carboxylate esters are the desired reaction products, silane reduction of the carbonyl compound in the presence of a carboxylic acid gives the ester directly when a mineral acid catalyst is used (Table I). Modification of these reaction conditions may be useful in preparing other alcohol derivatives and alkyl halides in one step from an aldehyde or ketone.

Poly(methylsiloxane) (PMS) was unsuitable as a reducing agent in attempts to produce symmetrical ethers from aldehydes. Under reaction conditions that gave high yields of symmetrical ethers in rapid reductions of heptanal and dodecanal by triethylsilane, reduction by PMS was slow and gave mixtures of alcohol and ether.

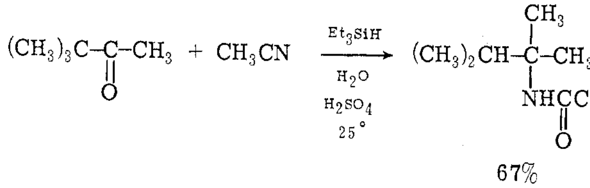
Preparation of Acetamides. Reductions of ketones and aryl aldehydes by triethylsilane in acetonitrile using aqueous sulfuric acid give N-substituted acetamides in good yields (eq 3) and provide a convenient method for the introduction of an amino functionality onto a hydrocarbon skeleton. Yields of products from reductions of representative carbonyl compounds are given in Table IV. Only ali-

$$R_2C{=}O + Et_3SiH + CH_3C{\equiv}N + H_2O \xrightarrow{H^+} R_2CHNHCOCH_3 + Et_3SiOSiEt_3 \quad (3)$$

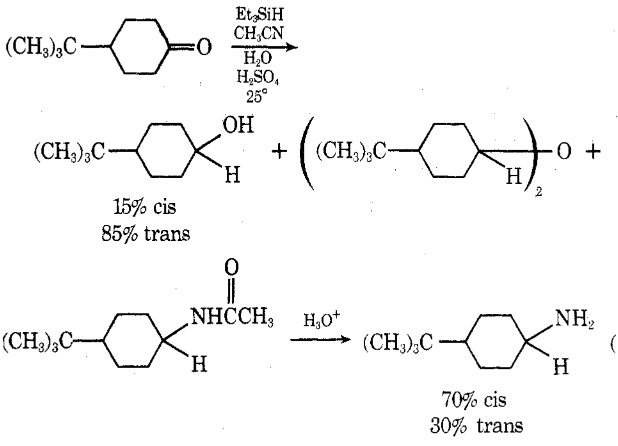
phatic aldehydes did not form amides under the reaction conditions used. Significantly lower isolated yields of amide products (15–20%) were obtained when the reactions were run in 67% aqueous sulfuric acid rather than in the 75% aqueous sulfuric acid solutions reported in Table IV.

The acetonitrile solution of aqueous sulfuric acid is suitable to convert alcohols to acetamides by the Ritter reaction.[10] Under the same reaction conditions used for the reductive transformation of carbonyl compounds to acetamides, but without added silane, benzyl alcohol and *exo*-bicyclo[2.2.1]heptan-2-ol gave *N*-benzylacetamide and *N*-(*exo*-bicyclo[2.2.1]hept-2-yl)acetamide in 71 and 73% isolated yield, respectively. Cyclohexanol gave a mixture of *N*-cyclohexylacetamide (16%) and cyclohexyl ether (18%) indicating both incomplete reaction and competitive formation of symmetrical ether. The reaction conditions employed are milder than those generally used for the Ritter reaction[11] and, with the exception of cyclohexanol in this study, are preferable for acetamide formation.

Only the rearranged product was observed when 3,3-dimethyl-2-butanone was reduced by triethylsilane in an acetonitrile solution of aqueous sulfuric acid (eq 4), indicating that reduction precedes the Ritter reaction and that the alcohol produced by silane reduction (see Table I) undergoes carbon-skeleton rearrangement in the formation of the acetamide product. Under the same reaction conditions described in Table IV for cyclohexanone, 4-*tert*-butylcyclohexanone gave a mixture of products (eq 5) consisting of 4-*tert*-butylcyclohexene (4%), unrearranged alcohols and symmetrical ethers (70%), and acetamides (21%). The ratio of cis to trans alcohol was 15:85; and all stereochemical combinations of ethers, cis,cis, cis,trans, and trans,trans, were observed. Hydrolysis of the isomeric *N*-(4-*tert*-butylcyclohexyl)acetamides gave the corresponding amines.



$$(CH_3)_3C-\underset{\underset{O}{\|}}{C}-CH_3 + CH_3CN \xrightarrow[\substack{H_2O\\H_2SO_4\\25^\circ}]{Et_3SiH} (CH_3)_2CH-\overset{\overset{CH_3}{|}}{\underset{\underset{NH\underset{\underset{O}{\|}}{C}CH_3}{|}}{C}}-CH_3 \qquad 67\% \qquad (4)$$



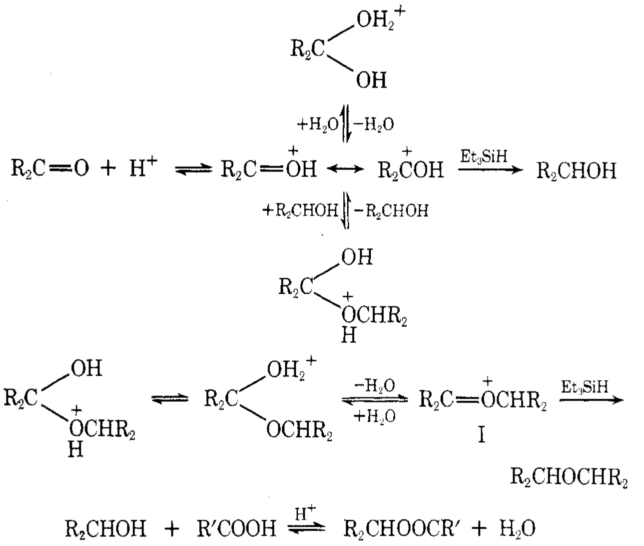
(5)

Discussion

In acidic media aldehydes and ketones are converted by silane reduction to alcohols, symmetrical ethers, unsymmetrical ethers,[12] carboxylate esters, or acetamides in good yields. The nature of the product is highly dependent on the reaction conditions used for the reduction. In aqueous acidic solutions alcohols are formed when a solvent such as acetonitrile, sulfolane, or ethyl ether is used; unsymmetrical ethers predominate in alcoholic acidic media.[12] Symmetrical ethers form in competition with alcohols in aqueous acidic media and in competition with carboxylate esters in carboxylic acid solutions.

The interrelated processes for alcohol, carboxylate ester, and ether formation can be explained by the mechanism described in Scheme I. Reduction occurs in acidic media even when less than an equivalent amount of acid is employed. When a sufficient amount of water is present in the reaction medium, the protonated carbonyl compound is present in equilibrium with its hydrate; under such conditions the alcohol is the predominant reaction product. When the amounts of mineral acid and water are comparable, the yield of alcohol reflects the molar excess of water; thus, when benzaldehyde is reduced by triethylsilane using sulfuric acid (Table I) no alcohol was formed when concentrated sulfuric acid was used, 32% benzyl alcohol was produced when the molar ratio of water to sulfuric acid was 1.5:1.0 (67% aqueous sulfuric acid), and with the molar ratio of water to sulfuric acid at 3.0:1.0, the relative yield of benzyl alcohol was 88%. Comparable results for alcohol formation were obtained with concentrated hydrochloric acid and aqueous sulfuric acid at similar molar ratios of water to acid.

Scheme I



Ether formation is explained by reduction of the oxonium ion (I) formed from the nucleophilic addition of alcohol to the protonated carbonyl compound followed by elimination of a molecule of water. Such as intermediate, formed independently, has been reduced by trialkylsilanes to a symmetrical ether.[13]

In carboxylic acid media the production of carboxylate ester competes with symmetrical ether formation. The relative yields of ether and ester formed in the reduction of substituted benzaldehydes in trifluoroacetic acid reflects the relative basicity of the carbonyl compound. The yield of symmetrical ether increases with decreasing acidity of the conjugate acid of para-substituted benzaldehydes: *p*-$NO_2C_6H_4CHO$ ($pK_a = -8.45$,[14] 32% ether), *p*-ClC_6H_4CHO ($pK_a = -7.26$,[14] 80% ether), and C_6H_5CHO ($pK_a = -7.10$,[14] 89% ether). Additionally, ether formation is favored over the formation of trifluoroacetate esters in polar solvents; the relative yield of benzyl ether from the reduction of benzaldehyde using limited amounts of trifluoroacetic acid was 49% in carbon tetrachloride and 96% in acetonitrile (Table II). These results are consistent with the involvement of I in the production of symmetrical ethers; the mechanism of esterification does not involve a comparable substituent-sensitive intermediate.[15]

Ether formation is also sensitive to steric effects. Despite the greater basicity of ketones compared to aldehydes,[16] aldehydes gave higher relative yields of symmetrical ethers than did ketones under comparable reaction conditions. Additionally, 1-naphthaldehyde ($pK_a = -6.34$)[17] gave 67% of the corresponding symmetrical ether whereas the less basic 2-naphthaldehyde ($pK_a = -6.68$)[17] yielded 84% of the less sterically hindered symmetrical ether.

The necessity of using a reaction solvent such as acetonitrile to prevent ether formation in the preparation of alcohols can be explained as being due to the insolubility of the carbonyl compound, alcohol, and triethylsilane in the aqueous solution. The reaction solvent provides a medium for protecting the alcohol product from nucleophilic addition to the carbonyl group leading to ether formation. In *N,N*-dimethylformamide protonation of the amide[16] prevents protonation of the carbonyl group.

The results obtained from the reduction of benzaldehyde by triethylsilane using trifluoroacetic acid (Figure 1) show that the rate of symmetrical ether formation from aldehydes is rapid compared to ester formation during the first half-life. Only as the concentration of the aldehyde decreases in the second half-life does ester formation become important. Since the amount of benzyl alcohol and benzyl triethylsilyl ether remains relatively constant with time as the yields of both benzyl ether and benzyl trifluoroacetate increase, the rate of hydride transfer to I must be at least as fast as the corresponding reduction of protonated benzaldehyde.[18]

In ketone reductions steric factors decrease the relative rate of ether formation compared to ester formation. The production of symmetrical ethers is favored by low temperatures and a low concentration of acid (Table III). The effect of acid concentration on the relative yield of ether in silane reductions in trifluoroacetic acid is not nearly so dramatic in aldehyde reductions as in ketone reductions.

One advantage of silane reductions of carbonyl compounds in acidic media is that the alcohol product can be made to undergo subsequent acid-catalyzed reactions in the same reaction medium. This potential for use in organic synthesis is evident in the formation of carboxylate esters from aldehydes and ketones and is indicated by the formation of benzyl chloride in the reduction of benzaldehyde by triethylsilane using concentrated hydrochloric acid. The versatility of this reduction method is shown by the coupling of the Ritter reaction to the silane reduction reaction in the preparation of acetamides from ketones and aryl aldehydes.

Silane reduction precedes the Ritter reaction. Those alcohols formed by reduction that normally undergo the Ritter reaction[10] form N-substituted amides in the coupled sequence. Water is necessarily used in the reaction medium to favor the formation of alcohol rather than ether in the reduction reaction; without water ether formation becomes an important process (Table I). The concentration of sulfuric acid is higher than that normally used for alcohol formation in silane reductions of aldehydes and ketones.

Structural rearrangement is observed in the formation of amides in the silane reduction–Ritter reaction sequence. The reaction conditions employed, however, do not favor the extensive degree of rearrangement observed when concentrated sulfuric acid is used. We find that 4-*tert*-butylcyclohexanone gives *N*-(4-*tert*-butylcyclohexyl)acetamide without rearrangement in 75% aqueous sulfuric acid; 4-methylcyclohexanol, on the other hand, has been shown to yield only rearranged products in the Ritter reaction in concentrated sulfuric acid.[19]

The reduction of 4-*tert*-butylcyclohexanone by triethylsilane using aqueous sulfuric acid under milder conditions than those reported for acetamide formation gave 4-*tert*-butylcyclohexanol in an isomeric distribution of 30% cis and 70% trans alcohol. This isomeric distribution does not noticeably change when the acid strength is varied.[18] The ratio of isomeric amines formed by hydrolysis of the corresponding amides is, however, significantly different from the isomeric ratio of alcohols. Although only one experiment is reported here, the results indicate that the cis alcohol reacts faster in the Ritter reaction than the trans alcohol and that axial attack by acetonitrile is preferred over equitorial attack in the formation of *N*-(4-*tert*-butylcyclohexyl)acetamides. The greater reactivity of *cis*-4-*tert*-butylcyclohexylderivatives has been previously observed in solvolytic studies.[20] The preference for axial bond formation in reactions of 4-*tert*-butylcyclohexyl cations has also been described.[21]

Experimental Section

General. Instrumentation has been previously described.[22] Use was made of 10-ft columns of 10% Carbowax 20M and 5-ft columns of 20% Carbowax 20M on Chromosorb P and 5-ft columns of 3% SE-30 on Varaport 30. Melting points and boiling points were uncorrected. Aldehydes, ketones, tri-*n*-hexylsilane, tetramethyldisiloxane, and triethylsilane, were commercially available and used without further purification. Triethysilanol and hexaethyldisiloxane were prepared by conventional methods.[2,23]

***n*-Butylsilane** was prepared by lithium aluminum hydride reduction of commercially available *n*-butyltrichlorosilane. *n*-Butyltrichlorosilane (192 g, 1.00 mol) was added dropwise over a 1.5-hr period to an ice–water bath cooled mixture of lithium aluminum hydride (36.0 g, 0.95 mol) in 350 ml of *n*-butyl ether. The constantly stirred mixture was contained in a 1-l., three-necked flask equipped with a condenser, drying tube, addition funnel, and mechanical stirrer. After addition was complete the flask was warmed to room temperature, and stirring was continued for an additional 1 hr. Distillation through a 2-ft Vigreux column gave 80.5 g (0.91 mol, 91% yield) of *n*-butylsilane, bp 55–58°. Redistillation gave *n*-butylsilane with bp 54–56° (lit.[24] bp 56°); pmr (neat) δ 3.53 (t, 3 H), 1.65–1.1 (m, 4 H), and 1.1–0.5 (m, 5 H); ir (neat) 2130 cm^{-1} (Si-H stretch).

Triethylsilane Reductions of Aldehydes and Ketones in Aqueous Acidic Media. In a typical reaction the carbonyl compound and triethylsilane were weighed into a round-bottom flask, and the appropriate amount of organic solvent was added. The premixed acid–water solution was then slowly added to the reaction flask at room temperature. Stirring was effected at a uniform and rapid rate using a magnetic stirrer. The reaction was allowed to proceed at room temperature. For all experiments in which aqueous mineral acid-acetonitrile or sulfolane was used the reaction mixture was heterogeneous. With the exception of anthroquinone the carbonyl compounds were soluble in the reaction media. An aliquot of the reaction solution was removed for pmr analysis prior to work-up to determine the extent of reduction. This aliquot generally yielded the same results for relative product yield as analysis of the product mixture after work-up, indicating that the work-up procedure did not selectively retain or remove a particular reduction product.

After reduction was complete the reaction solution was diluted with 25 ml of a saturated sodium chloride solution, and 25 ml of ether was added. The resultant layers were separated after thorough mixing, and the aqueous solution was washed twice with 25-ml portions of ether. The combined ether solution was washed with 25-ml portions of water and saturated sodium bicarbonate and was passed through anhydrous magnesium sulfate. The ether was removed by distillation at atmospheric pressure. Isolated yields of reduced products averaged 80% in small-scale reductions (5–10 mmol). Silane products were not separated from the organic products by this extraction method.

Each product mixture was analyzed from its pmr spectrum; yields were calculated from averaged integrations of proton absorptions by comparison to an internal standard. Reproducibility was shown to be ±2% in duplicate runs. The yields of products for several reactions were also obtained by glpc analysis; these results were nearly identical with those obtained by pmr analysis. Prod-

Table V
Reduction of Benzaldehyde by Tri-*n*-hexylsilane in Carbon Tetrachloride–Trifluoroacetic Acid at 40°

	Relative % yield			
Time, min	C_6H_5CHO	$C_6H_5CH_2O_2CCF_3$	$(C_6H_5CH_2)_2O$	$C_6H_5CH_2OH$ + $C_6H_5CH_2OSi(Hex)_3$
10	51	1	34	15
15	44	5	36	15
20	41	6	38	15
25	37	8	40	15
30	35	9	41	15
35	31	12	42	15
40	26	15	44	15
45	25	16	44	15
55	22	19	44	15

ucts were identified from their pmr spectra by comparison to authentic samples and by observing signal enhancements when a small amount of the known was added to the pmr sample. With the exception of 2-propanol, which was not isolated, alcohol products were additionally confirmed by glpc or ir identification methods.

Silane Reductions in Ether–Aqueous Sulfuric Acid Media. The reduction of cyclooctanone exemplifies the procedure used. To 6.3 g (50 mmol) of cyclooctanone and 2.2 g (25 mmol) of *n*-butylsilane in 6 ml of ethyl ether was added 3.5 ml of 73 g % aqueous sulfuric acid. The reaction mixture was heterogeneous, and the reaction was slightly exothermic. After rapidly stirring overnight the acid was neutralized by adding an excess of 10% aqueous sodium hydroxide, and the mixture was extracted with four 20-ml portions of ethyl ether. The combined ether extracts were dried over potassium hydroxide and filtered, and the ether was removed under reduced pressure. The residue was distilled giving 4.9 g (39 mmol, 78% yield) of cyclooctanol, bp 92–93° (23 Torr) [lit.[25] bp 99° (16 Torr)]. Only a small amount of pot residue remained after the distillation.

Reduction of octanal by *n*-butylsilane followed by extraction and distillation gave 1-octanol in 31% yield and 1-octyl ether in 61% yield. With tetramethyldisiloxane 1-octanol and 1-octyl ether were formed in 50 and 50% yield, respectively; using a lower acid concentration (37 g % aqueous sulfuric acid), the relative yield of alcohol was increased to 65%.

Silane Reductions of Aldehydes and Ketones in Carboxylic Acid Media. In a typical reaction the carbonyl compound and silane were weighed into a round-bottom flask and the reaction solvent, if different from the carboxylic acid, was added. The carboxylic acid was added last, and the resultant homogeneous solution was stirred at room temperature with a magnetic stirrer. Aliquots were removed at appropriate times and subjected to pmr analysis to determine the extent of reduction. Products were identified from the pmr spectra of the reaction solutions by comparison with authentic samples, when available; relative yields of products were determined from averaged integrations of the individual and characteristic absorption signals of each compound through reference to an internal standard. Ethers were generally isolated by direct distillation of the reaction mixture under reduced pressure. 2-Naphthyl ether was insoluble in trifluoroacetic acid and was filtered and recrystallized. Isolated ethers were identified from their pmr spectra and by comparison of boiling or melting points with the literature values.

p-Toluyl ether was obtained in 91% yield from the reduction of *p*-tolualdehyde (5.0 mmol) by triethylsilane (6.0 mmol) using 0.25 equiv of concentrated sulfuric acid in 2.5 ml of acetonitrile. Reaction time was 5 days.

Cyclohexyl ether was prepared by reduction of cyclohexanone (3.92 g, 40 mmol) with *n*-butylsilane (1.78 g, 20 mmol) in trifluoroacetic acid. The acid (75 mmol) was added slowly over a period of 1 hr to the reaction mixture cooled at −35°. After complete addition the reaction flask was placed in a freezer at −15° for 70 hr. Direct distillation gave 2.91 g (16 mmol, 80% yield) of cyclohexyl ether, bp 119–121° (18 Torr) [lit.[26] bp 97–98.5° (8 Torr)].

Reduction of Benzaldehyde in Carbon Tetrachloride–Trifluoroacetic Acid. Product Yields with Time. Benzaldehyde (5.0 mmol) and trifluoroacetic acid (10.0 mmol) were weighed into a round-bottom flask, and carbon tetrachloride (2.5 ml) was added. The solution was heated to 40 ± 1° and the silane (5.0 mmol) was added. An aliquot was removed from the homogeneous reaction solution after thorough mixing, and a pmr spectrum was taken of the sample. Proton absorptions were integrated, and the integrations were repeated every 5 min over a reaction period of 1 hr. The reaction temperature was maintained at 40°. The results with triethylsilane are described graphically in Figure 1. Data for the reduction of benzaldehyde with tri-*n*-hexylsilane are given in Table V. Reduction of benzaldehyde by diphenylsilane was at least 20 times slower than the corresponding reduction by either triethylsilane or tri-*n*-hexylsilane.

Preparation of Acetamides. To the carbonyl compound (60 mmol) and triethylsilane (66 mmol) in 15 ml of acetonitrile was added 3.0 ml of water followed by 9.0 ml of concentrated sulfuric acid. Sulfuric acid was added slowly to the reaction solution cooled in an ice bath; the acid addition was exothermic. The heterogeneous reaction mixture was stirred rapidly at room temperature for between 48 and 72 hr. The reaction was quenched by adding 30 ml of 50% aqueous sodium hydroxide, and the aqueous mixture was extracted three times with 50-ml portions of methylene chloride. The combined methylene chloride extract was passed through anhydrous magnesium sulfate, and the methylene chloride was removed under reduced pressure. With the exception of the norcamphor and benzophenone reduction products the product mixtures were distilled under reduced pressure to give hexaethyldisiloxane and amides in separate fractions. In the cyclohexanone reduction cyclohexyl ether and *N*-cyclohexylacetamide were collected in the same fraction; *N*-cyclohexylacetamide was separated from the ether by recrystallization. The product mixtures from the benzophenone and norcamphor reductions were washed three times with pentane to remove hexaethyldisiloxane and other soluble reaction products. The solid amide products were recrystallized from ether and characterized by pmr analysis and by their melting points through comparison to authentic samples or literature values. Isolated yields of acetamides from reactions with benzaldehyde, cyclohexanone, and norcamphor were 15–20% lower when 6 ml of concentrated sulfuric acid was used instead of 9 ml in the above procedure owing to incomplete reaction of the reduced carbonyl compound.

The same procedure was used for the Ritter reaction with the exception that the alcohol was used instead of the carbonyl compound and no triethylsilane was added.

3,3-Dimethyl-2-butanone (5.0 mmol) was reduced by triethylsilane (10.0 mmol) using 1.5 ml of 67% aqueous sulfuric acid and 2.5 ml of acetonitrile. The product mixture from the reduction was analyzed by pmr spectroscopy and by glpc methods. Only one amide product other than acetamide was observed; this product was collected by glpc and characterized as *N*-2-(2,3-dimethylbutyl)acetamide by pmr and ir spectroscopy and from its melting point by comparison to the literature value.

Reduction of 4-*tert*-Butylcyclohexanone in an Acetonitrile Mixture with Aqueous Sulfuric Acid. Reaction occurred as previously described. After work-up pmr analysis was used to give the relative yields of reaction products. Alcohol and other products were additionally characterized and the relative yields of the isomeric alcohols were determined by glpc analysis through comparison with authentic samples. Refluxing the reaction products overnight with 50% aqueous sulfuric acid, followed by work-up, gave the isomeric 4-*tert*-butylcyclohexylamines, which were analyzed by pmr spectroscopy and by glpc.

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Registry No.—Triethylsilane, 617-86-7; *n*-butylsilane, 1600-29-9; *n*-butyltrichlorosilane, 7521-8-4; tetramethyldisiloxane, 30110-74-8; tri-*n*-hexylsilane, 2929-52-4; 4-*tert*-butylcyclohexanone,98-53-3.

Supplementary Material Available. Additional data for Tables I and II will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-2740.

References and Notes

(1) (a) Part II: C. T. West, S. J. Donnelly, D. A. Kooistra, and M. P. Doyle, *J. Org. Chem.*, **38**, 2675 (1973); (b) Camille and Henry Dreyfus Foundation Teacher–Scholar Grant Awardee, 1973–1978; (c) National Science Foundation Undergraduate Research Participant, summer 1972; (d) National Science Foundation Undergraduate Research Participant, summer 1971.

(2) H. H. Anderson, *J. Amer. Chem. Soc.*, **80**, 5083 (1958).

(3) G. G. Hess, F. W. Lampe, and L. H. Sommer, *J. Amer. Chem. Soc.*, **87**, 5327 (1965).

(4) (a) D. N. Kursanov, Z. N. Parnes, V. A. Tsyryapkin, and R. V. Kudryavtsev, *Dokl. Akad. Nauk SSSR*, **202**, 874 (1972), and previous papers in this series; (b) F. A. Carey and H. S. Tremper, *J. Org. Chem.*, **36**, 758 (1971), and previous papers in this series.

(5) V. I. Zdanovich, R. V. Kudryavtsev, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 472 (1970).

(6) R. Calas, N. Duffant, and C. Bardot, *C. R. Acad. Sci.*, **249**, 1682 (1959).

(7) (a) R. A. Benkeser and W. E. Smith, *J. Amer. Chem. Soc.*, **91**, 1556 (1969; (b) R. A. Benkeser, *Accounts Chem. Res.*, **4**, 94 (1971).

(8) (a) R. Calas, E. Frainnet, and J. Bonastre, *C. R. Acad. Sci.*, **251**, 2987 (1960); (b) I. I. Lapkin, T. N. Povarnitsyna, and L. A. Kostareva, *Zh. Obshch. Khim.*, **38**, 1578 (1968), and previous articles in this series.

(9) D. N. Kursanov, Z. N. Parnes, G. I. Bassova, N. M. Loim, and V. I. Zdanovich, *Tetrahedron*, **23**, 2235 (1967).

(10) L. I. Krimen and D. J. Cota, *Org. React.*, **17**, 213 (1969).

(11) G. Glikmans, B. Torck, M. Hellin, and F. Coussemant, *Bull. Soc. Chim. Fr.*, 1376 (1966), have reported that alcohols require concentrated sulfuric acid.

(12) M. P. Doyle, D. J. DeBruyn, and D. A. Kooistra, *J. Amer. Chem. Soc.*, **94**, 3659 (1972).

(13) M. P. Doyle, M. A. Zaleta, J. E. DeBoer, and W. Wierenga, *J. Org. Chem.*, **38**, 1663 (1973).

(14) K. Yates and R. Stewart, *Can. J. Chem.*, **37**, 664 (1959).

(15) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(16) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

(17) G. Culbertson and R. Petit, *J. Amer. Chem. Soc.*, **85**, 741 (1963).

(18) In subsequent publications we will discuss in detail the mechanism and stereochemistry of the hydride transfer step in silane reductions.

(19) R. Jacquier and H. Christol, *Bull. Soc. Chim. Fr.*, 600 (1957).

(20) D. S. Noyce, B. E. Johnston, and B. Weinstein, *J. Org. Chem.*, **34**, 463 (1969); S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955).

(21) S. D. Elakovich and J. G. Traynham, *J. Org. Chem.*, **38**, 873 (1973).

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

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

(24) H. E. Opitz, J. S. Peake, and W. H. Nebergall, *J. Amer. Chem. Soc.*, **78**, 292 (1956).

(25) O. Wallach, *Justus Liebigs Ann. Chem.*, **353**, 318 (1907).

(26) R. Willstatter, *Ber.*, **45**, 1466 (1912).

Reduction Products in Copper(I)-Promoted Diazonium Ion Reactions. Hydrogen Abstraction from Amines Coordinated to Copper(I), from Water, and from Transient Radicals

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Reduction products are observed in amine–copper(I) perchlorate promoted decomposition of aryldiazonium salts when the amine ligands are capable of hydrogen atom donation. The effective reducing agents evidently are the complexed rather than the free ligands, *i.e.*, the tris(amine)copper(I) cation in the case of tetra- and tricoordinated salts and the bis(amine)copper(I) cation in the dicoordinated systems. In the presence of excess ligand a new product is obtained, which is probably an ammonium salt formed from the amine and the incipient aryl cation. In the absence of hydrogen-donating ligands it has been shown that the small but consistent amount of benzophenone formed in the copper(I)-promoted decomposition of 2-diazobenzophenone tetrafluoroborate arises from (a) the precursor to 9-fluorenone and (b) the solvent, water. Hydrogen atom abstraction from both these sources is rate determining and subject to a kinetic isotope effect. Since water is a notoriously poor hydrogen atom donor, transfer of a hydrogen atom from the aquated coordination sphere of copper(I) *via* a bridged intermediate is postulated.

In the course of our investigations of copper(I) oxide and copper(I) perchlorate decompositions of aryldiazonium tetrafluoroborates,[2] it was noted that reduction products were consistently produced. A thorough study of the hydrogen source in these decompositions was, therefore, undertaken.

The tetrafluoroborate salt of 2-diazobenzophenone (1) was selected for this purpose because of the large amount of reliable data that were already available. This compound, as are all aromatic diazonium compounds, is capable of cleaving homolytically and/or heterolytically, depending on conditions. The decomposition of 2-diazobenzophenone tetrafluoroborate (1) was first carried out by Graebe and Ullman,[3] who found that 1 could be converted into 9-fluorenone (4). DeTar and Relyea[4] showed the formation of *o*-hydroxybenzophenone (3, Z = OH) along with 9-fluorenone (4) in the system, in the presence and absence of a copper catalyst. Lewin and Cohen[5a] then elucidated conditions under which homolytic and heterolytic cleavage of the carbon–nitrogen bond occurred. They found that thermal decomposition of diazonium salts in acidic solution produced phenyl cations, whereas the room temperature reaction, with a catalyst, led to a phenyl radical. Their proposed mechanism of the copper(I)-catalyzed decomposition of 2-diazobenzophenone tetrafluoroborate seemed to hold for amine–copper(I) perchlorate promoted decompositions with the addition of dimerization of radical A.[2] Thus, it has been shown that good yields of the phenol (3, Z = OH) can be obtained in the presence of a large excess of cupric ion and that benzophenone (2) is produced in the presence of hydrogen donors such as acetone and ethanol.[2] However, benzophenone was formed in both the copper(I) oxide and the amine–copper(I) perchlorate promoted reactions even in the absence of such hydrogen donors. A similar observation had been previously made[5a] and several possible pathways for benzophenone (2) formation were considered in conjunction with the proposed reaction scheme;[5a] the authors concluded, however, that "the nature of the reducing agent remains obscure." See Scheme I.

Results and Discussion

Reduction Products. A. In Amine–Copper(I) Perchlorate Promoted Reactions. Benzophenone (2) was formed in amine–copper(I) perchlorate promoted decom-