

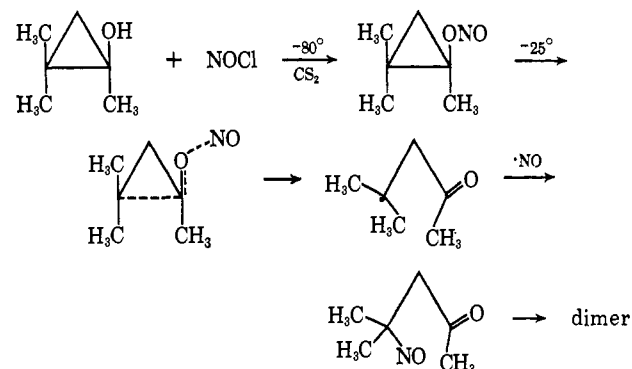
Table I. Decomposition Temperatures of Cyclopropyl Nitrites ($t_{1/2} \sim 1$ hr)

Nitrite ^a	Temp, °C	Product
2,2,3,3-Tetramethyl-1-methoxycyclopropyl	< -80	(CH ₃) ₂ C(NO)C(CH ₃) ₂ CO ₂ CH ₃
2,2,3,3-Tetramethylcyclopropyl	-55	(CH ₃) ₂ C(NO)C(CH ₃) ₂ CHO
1,2,2,3,3-Pentamethylcyclopropyl ^b	-45	(CH ₃) ₂ C(NO)C(CH ₃) ₂ COCH ₃
1,2,2-Trimethylcyclopropyl	-25	[(CH ₃) ₂ C(NO)CH ₂ COCH ₃] ₂
<i>trans</i> -2-Phenylcyclopropyl	-20	3-Phenyl-5-hydroxy-2-isoxazoline ^d
<i>trans,trans</i> -2,3-Dimethyl-1-phenylcyclopropyl	-5	[CH ₃ CH(NO)CH(CH ₃)COC ₆ H ₅] ₂
Cyclopropyl ^c	>0	5-Hydroxy-2-isoxazoline ^d
1-Phenylcyclopropyl ^c	>0	(ONCH ₂ CH ₂ COC ₆ H ₅) ₂
1-Methylcyclopropyl ^c	+20	(ONCH ₂ CH ₂ COCH ₃) ₂

^a The nitrites were formed from the corresponding alcohols and nitrosyl chloride, at low temperatures. ^b The starting alcohol was synthesized by methyl lithium treatment of the hemiketal. ^c See ref 6 for the preparation of the corresponding cyclopropanol. ^d These products can be visualized as cyclization products of the intermediate nitroso ketone, although the ketone has not been detected in the nmr.

4-nitroso-4-methyl-2-pentanone which was identified by comparison with an authentic sample.⁵

Scheme I



The temperature at which rapid decomposition of a cyclopropyl nitrite ester occurs correlates well with the radical-stabilizing ability of the 2 substituents (see Table I). Thus, the 1,2,2-trimethyl and the *trans*-2-phenyl⁶ esters decompose near -25°, the isomeric 2,3-dimethyl-1-phenylcyclopropyl nitrites⁷ decompose at -5°, while 1-methylcyclopropyl nitrite and nitrite esters of other cyclopropanols without 2 substituents are stable until near room temperature. Nitrite esters of 2,2,3,3-tetramethylcyclopropanols⁸ are particularly unstable, the parent ester decomposing at -55° and the 1-methoxy derivative at -80°. Nitrite esters of ordinary alcohols undergo thermolysis only at elevated temperatures (150–200°), and the rates of their decomposition are not ordinarily sensitive to structure.⁹

The conversion of the cyclopropanols to the corresponding nitrite esters and their subsequent decompositions proceed in high yield. The nitroso ester from 2,2,3,3-tetramethyl-1-methoxycyclopropyl nitrite and the nitroso ketone from 1,2,2,3,3-pentamethylcyclopropyl nitrite can be isolated in >90% yield. In the other examples, no significant by-products were observed by nmr.

The alkyl radical intermediates in the cyclopropyl nitrite decompositions can readily be trapped. For

(5) J. G. Aston, D. F. Menard, and M. G. Mayberry, *J. Chem. Soc.*, 1530 (1932).

(6) The cyclopropanol was prepared in the manner described by C. H. DePuy, G. M. Dappen, K. L. Eilers, and R. A. Klein, *J. Org. Chem.*, **29**, 2813 (1964).

(7) The preparations of the corresponding cyclopropanols have been described; see ref 3.

(8) N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *J. Amer. Chem. Soc.*, **87**, 2613 (1965); N. J. Turro, W. B. Hammond, P. A. Leermakers, and H. Thomas, *Chem. Ind. (London)*, 990 (1965).

(9) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

example, ether solutions of the pentamethyl nitrite and its 1-methoxy analog were prepared, at -80°, in the presence of 10 equiv of bromotrichloromethane and allowed to decompose slowly in the dark. Subsequent analysis of the nmr spectra of the products indicated *ca.* 40:60 mixtures of the ring-opened nitroso compounds and the corresponding β -bromo carbonyl compounds. The bromo compounds were identical with those obtained by reaction of the appropriate cyclopropanol with brominating agents.

We anticipate that the low-temperature thermolysis of these esters will allow us to study the stereochemistry, spectra, and reactivity of a number of alkyl radicals, and experiments along these lines are already under way. We intend also to compare the nature of the radicals formed thermally with those formed by the photochemical decomposition of these same nitrites, a reaction which also occurs readily.¹⁰

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(10) H. L. Jones, unpublished results.

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Trichlorosilane-Tertiary Amine Combinations as Reducing Agents for Polyhalo Compounds. Potential Analogies with Phosphorus Chemistry

Sir:

The effectiveness of organic bases as catalysts for the addition of trichlorosilane to acrylonitrile¹ and phenylacetylene^{2,3} is suggestive of a little-explored aspect of organosilicon chemistry. In the course of our experiments in this area, we have discovered that in the presence of tertiary amines trichlorosilane undergoes facile reaction with a variety of organic halides, yielding products that are significant from both synthetic and mechanistic standpoints. Reported here is a series of reactions in which polyhalo compounds are reduced cleanly and selectively by the trichlorosilane-amine combination. The data are summarized in Table I.

(1) S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Japan*, **29**, 322 (1956).

(2) R. A. Pike, *J. Org. Chem.*, **27**, 2186 (1962).

(3) R. A. Benkeser, S. Dunny, and P. R. Jones, *J. Organometal. Chem. (Amsterdam)*, **4**, 338 (1965).

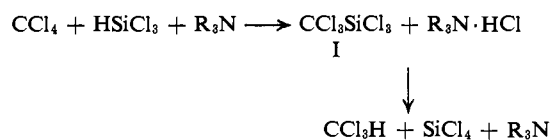
Table I. Reduction of Polyhalo Compounds with Trichlorosilane-Tertiary Amines

Run	Reactants (mole ratios)	Conditions	Products
1	CCl ₄ -HSiCl ₃ (1:1.5)	0.2 equiv ^c of (<i>n</i> -C ₄ H ₉) ₃ N, neat, 20 hr, 40–60°	CHCl ₃ (82%), ^a SiCl ₄
2	BrCCl ₃ -HSiCl ₃ (1:1.25)	0.2 equiv of (<i>n</i> -C ₄ H ₉) ₃ N, CH ₂ Cl ₂ (solvent), 2 hr, 48–50°	CHCl ₃ (quantitative), ^a BrSiCl ₃
3	CCl ₃ COOCH ₃ -HSiCl ₃ (1:1.25)	Same as above	HCCl ₂ COOCH ₃ (82%), ^b SiCl ₄
4	CCl ₃ COCH ₃ -HSiCl ₃ (1:1.25)	1 equiv of (<i>n</i> -C ₄ H ₉) ₃ N, THF, 1 hr, 68–69°	HCCl ₂ COCH ₃ (80%), ^b SiCl ₄
5	CCl ₃ CCl ₃ -HSiCl ₃ -(<i>n</i> -C ₃ H ₇) ₃ N (1:1.25:1)	THF, 1 hr, 66–68°	Cl ₂ C=CCl ₂ (86%), ^b (<i>n</i> -C ₃ H ₇) ₃ N·HCl (97%), ^b SiCl ₄

^a Yield determined by quantitative vpc. ^b Yield of isolated product. ^c Based upon halocarbon used.

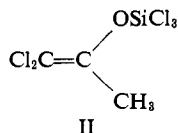
Carbon tetrachloride and trichlorosilane combined under the catalytic influence of tri-*n*-butylamine produced chloroform and silicon tetrachloride. When the reaction was carried out at low temperature in carbon tetrachloride solvent with a *full equivalent* of *N*-methyl-dicyclohexylamine, the amine hydrochloride (mp 193–195°) was precipitated quantitatively by pentane, and trichloromethyltrichlorosilane⁴ (I) melting at 113–114° after vpc purification was isolated in 40% yield. (*Anal.* Calcd for C₃SiCl₆: C, 4.75; Cl, 84.14; Si, 11.11. Found: C, 4.80; Cl, 84.50; Si, 10.84.) It is noteworthy that this same intermediate (and not trichloromethylbromodichlorosilane) was isolated in a similar experiment with bromotrichloromethane.

Seemingly, the reaction sequence for the reduction of carbon tetrachloride is as follows.



That I undergoes cleavage by tributylamine hydrochloride to give chloroform and silicon tetrachloride has already been demonstrated.⁵

The reductions of methyltrichloromethyl acetate (entry 3, Table I) and 1,1,1-trichloro-2-propanone (entry 4, Table I), while formally similar, have some important practical differences. Thus trichlorosilane and a *catalytic* amount of amine were sufficient to effect reduction of the ester to its dichloromethyl⁶ analog, which was isolated by direct distillation of the reaction mixture (bp 49–51° (11 mm)). In contrast, the initially vigorous reaction of 1,1,1-trichloro-2-propanone and trichlorosilane terminated when the amine “catalyst” was consumed. However, use of 1 equiv of tri-*n*-propylamine and subsequent precipitation of its hydrochloride with ether permitted isolation of the trichlorosilyl enol ether II, 1,1-dichloro-2-trichlorosilyloxypropene (bp 178°; ir bands at 6.08 (C=C) and 9.5–9.7μ



(SiO); nmr (CCl₄) δ 2.18 (s). *Anal.* Calcd for C₃H₃-

(4) P. DiGiorgio, L. H. Sommer, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 3512 (1948).

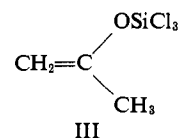
(5) G. D. Cooper and A. R. Gilbert, *ibid.*, **82**, 5042 (1960).

(6) R. Schiff, *Z. Phys. Chem.*, **1**, 378 (1887).

OSiCl₃: C, 13.84; H, 1.16; Cl, 68.07; Si, 10.79. Found: C, 13.70; H, 1.37; Cl, 67.84; Si, 10.53). Hydrolysis of II provided 1,1-dichloro-2-propanone.

A more convenient method for the direct preparation of the latter ketone entailed the use of 1 equiv of tri-*n*-butylamine with tetrahydrofuran as a solvent (Table I). Removal of the solvent (atmospheric pressure) accomplished the cleavage of compound II and removal of the silicon tetrachloride simultaneously. The dichloromethyl ketone⁷ (bp 119°) was then isolated by acid washing followed by distillation.

The spontaneous formation of 2-trichlorosilyloxypropene (III) (bp 111°; ir bands at 6.02 (C=C) and 9.3



μ (SiO); nmr (CCl₄) δ 4.52 (d, 1), 4.36 (m, 1), 1.93 (s, 3). *Anal.* Calcd for C₃H₅OSiCl₃: C, 18.81; H, 2.63; Cl, 55.54; Si, 14.67. Found: C, 19.07; H, 2.93; Cl, 55.23; Si, 14.96) when 1-chloro-2-propanone was combined with trichlorosilane and tri-*n*-butylamine in tetrahydrofuran (after 1 hr at 10–25° compound III was present in 72% yield, as determined by quantitative vpc) demonstrates that such enol ether formation is not restricted to polyhalo carbonyl compounds. Significantly, no silicon-carbon-bonded isomers (e.g., α-trichlorosilyl ketones) of II and III were detected.⁸

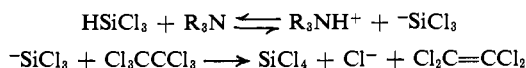
The rapid conversion of hexachloroethane to tetrachloroethylene (entry 5, Table I) and the formation of compounds like I, II, and III offer a striking parallel to the reaction of phosphines with similar halides,⁹ in which nucleophilic displacement on halogen is a central concept. The analogy with phosphine chemistry is particularly appealing in view of the isoelectronic relationship between the phosphines and the trichlorosilyl anion. Mechanisms based on the concept of a trichlorosilyl anion are attractive in these reactions in that they depict a highly nucleophilic species with a penchant for attack on halogen or oxygen. Accord-

(7) G. Borsche and R. Fittig, *Ann. Chem.*, **133**, 113 (1865).

(8) That stable silicon-carbon bonds can be formed in displacement reactions involving the trichlorosilane-tertiary amine combination will be disclosed in future publications.

(9) A. J. Speziale and C. C. Tung, *J. Org. Chem.*, **28**, 1353 (1963); R. Rabinowitz and R. Marcus, *J. Am. Chem. Soc.*, **84**, 1312 (1962); H. Hoffmann and H. J. Diehr, *Tetrahedron Letters*, 583 (1962); I. J. Borowitz, K. C. Kirby, Jr., and R. Virkhaus, *J. Org. Chem.*, **31**, 4031 (1966).

ingly, a simple interpretation of the reduction of hexachloroethane can be written. The other reactions re-



ported can be envisaged as occurring in similar ways.

The concept of a related chemistry between R_3P (and possibly $(\text{RO})_3\text{P}$) and silyl anions generated by base attack on the hydrogen of a silane ($-\text{SiH}$) has far reaching synthetic consequences for both the carbon and silicon chemist. Numerous experiments to extend the scope of these reactions and to establish their mechanisms are presently in progress in our laboratory.

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Acid Catalysis in Hydrofluoric Acid Buffers¹

Sir:

Aqueous solutions of hydrogen fluoride and its alkali metal salts possess a number of qualities desired of a good buffer system. The acid is moderately weak ($\text{p}K_a = 3.17$), its anion has low nucleophilic power, both acid and anion are stable toward oxidizing and reducing agents, and their solutions are transparent to visible and ultraviolet light, thus facilitating spectrophotometric measurement of reaction rates and equilibria. Hydrogen fluoride does attack glass vessels, but the present widespread availability of plastic laboratory ware has effectively removed this as a disadvantage. A more serious shortcoming stems from the fact that hydrofluoric acid buffers contain appreciable quantities of the species HF_2^- for which an acid catalytic power comparable to that of HF is claimed;² this would complicate kinetic analysis of reactions subject to general acid catalysis. We have recently discovered, however, that this complication is absent from a particularly simple example of this kind of reaction.

The hydrolysis of ethyl vinyl ether is known to occur through rate-determining proton transfer from a catalyzing acid to the substrate.³ This is also the first step of this reaction, and the process is not catalyzed by bases; rates of this hydrolysis, therefore, reflect the catalytic power of general acids in a particularly straightforward way. In order to assess the catalytic strengths of HF and HF_2^- in this system, we have carried out kinetic experiments under two sets of conditions: (1) in solutions prepared from hydrogen fluoride alone where the concentration of HF_2^- is negligibly low and the only effective catalysts are H_3O^+ and HF, and (2) in solutions containing added fluoride ion where the concentration of HF_2^- may be made

(1) This research was supported by a grant (GP 6580) from the National Science Foundation.

(2) R. P. Bell and J. C. McCoubrey, *Proc. Roy. Soc. (London)*, **A234**, 192 (1956).

(3) (a) P. Salomaa, A. Kankaapera, and M. Lajunen, *Acta Chem. Scand.*, **20**, 1790 (1966); (b) A. J. Kresge and Y. Chiang, *J. Chem. Soc., B*, **53**, 58 (1967); (c) M. M. Kreevoy and R. Eliason, *J. Phys. Chem.*, **72**, 1313 (1968).

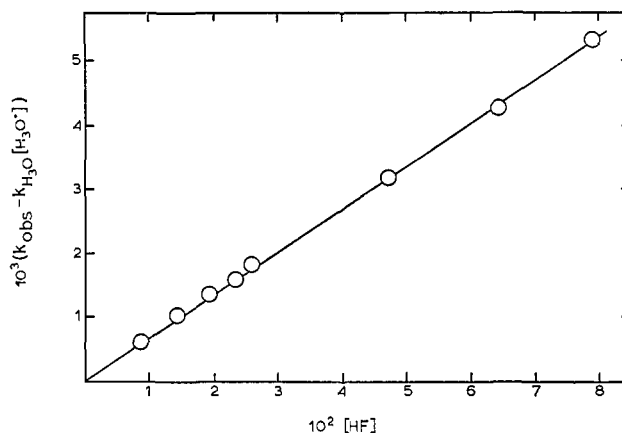


Figure 1. Dependence of $k_{\text{obs}} - k_{\text{H}_3\text{O}^+}[\text{H}_3\text{O}^+]$ on $[\text{HF}]$ for ethyl vinyl ether hydrolysis in HF solutions containing NaF; the line is drawn with slope = $6.71 \times 10^{-2} M^{-1} \text{sec}^{-1} (k_{\text{HF}})$ and designates expected behavior for catalysis by HF (and H_3O^+) alone. HF_2^- concentrations for the experimental points reading from left to right are (in units of $10^2 M$) 0.11, 0.54, 1.05, 1.66, 0.48, 1.55, 3.00, and 4.71.

comparable to that of HF. Using a value of $k_{\text{H}_3\text{O}^+}$ measured in dilute HClO_4 solutions ($1.75 \pm 0.02 M^{-1} \text{sec}^{-1}$ at 24.9°),⁴ we determined k_{HF} to be $(6.71 \pm 0.05) \times 10^{-2} M^{-1} \text{sec}^{-1}$ from the first set of experiments.⁵ However, when the latter was used to analyze data from the second series of measurements, in which HF_2^- concentrations ranged as high as 70% of HF concentrations, no excess rate assignable to catalysis by HF_2^- could be detected. This is demonstrated by Figure 1 where observed rate constants for this series, with contributions to reaction through H_3O^+ subtracted out ($k_{\text{obs}} - k_{\text{H}_3\text{O}^+}[\text{H}_3\text{O}^+]$), may be seen to agree remarkably well with rate constants calculated on the basis of the remaining reaction occurring through HF alone. (The latter is represented by the line in this figure.) Since $k_{\text{obs}} - k_{\text{H}_3\text{O}^+}[\text{H}_3\text{O}^+]$ in these experiments ranged from 60 to 90% of k_{obs} , and since rate constants could be measured with an accuracy of $\pm 1\%$, we estimate that reaction through HF_2^- , if not wholly absent, cannot amount to more than 2–3% of the reaction through HF.

This result prompted us to analyze the published data² for the only other reactions examined in this respect, the iodination of acetone and of acetylacetone. Our scrutiny revealed that the claim of equal catalytic powers for HF and HF_2^- rests on an error made in calculating the concentrations of the acidic species in these reaction mixtures.⁸ When appropriate corrections are made, catalysis by HF_2^- vanishes in the reaction of acetylacetone and is reduced to

(4) The value measured here is in good agreement with $k_{\text{H}_3\text{O}^+} = 1.77 M^{-1} \text{sec}^{-1}$ calculated from the known^{8b} temperature dependence of this reaction. Error limits used throughout this paper are standard deviations of mean values.

(5) Solution compositions were calculated throughout this work using $[\text{H}^+][\text{F}^-]/[\text{HF}] = 6.71 \times 10^{-4}/f_{\pm}$,⁶ $[\text{HF}_2^-]/[\text{HF}][\text{F}^-] = 3.86$,⁶ and $\log f_{\pm} = -0.50\mu^{1/2}/(1 + \mu^{1/2}) + 0.20\mu$,⁷ (this corresponds to the treatment used in ref 2), and were verified by indicator measurements of $[\text{H}^+]$ employing 2,4-dichloroaniline.

(6) H. H. Broene and T. DeVries, *J. Am. Chem. Soc.*, **69**, 1644 (1947); A. J. Ellis, *J. Chem. Soc.*, 4300 (1963).

(7) C. W. Davis, *ibid.*, 2093 (1938).

(8) Equation 5 of ref 2 is wrong: the coefficient of the second term on its right-hand side should be $1/2$ rather than $1/4$. This mistake produced significant errors in the analysis of rate data collected in the more acidic solutions of that work, but it did not materially affect the conclusions drawn concerning basic catalysis.