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Thermal Decomposition of Acrolein. The Attack of Methyl and *t*-Butoxy Free Radicals on Acrolein

BY C. E. CASTRO¹ AND F. F. RUST

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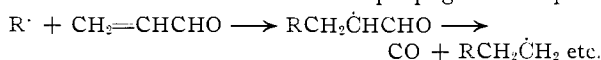
The thermolysis of gaseous solutions of acrolein in the 500–600° region yields principally carbon monoxide, ethylene, propylene, hydrogen, methane, ethane, 1,3-butadiene and 1-butene in decreasing order of importance. The results are rationalized in part by a short chain decomposition of the aldehyde through vinyl radicals for which the unstable acrylyl fragment is a precursor. Studies of the methyl radical induced decomposition of acrolein at 250° in the gas phase and the *t*-butyl hypochlorite photochlorination of the aldehyde at 22° in solution allow rough approximations of $k_{\text{addition}}/k_{\text{abstraction}}$ for methyl and *t*-butoxy free radicals to be made. These estimates are 4 and $1/18$ (max.), respectively.

Introduction

The literature abounds with the low temperature ionic chemistry of acrolein in solution. Very little attention, however, has been focused upon the high temperature behavior of this reactive aldehyde or upon its susceptibility toward free radical attack.

At 530°, in a static system, the decomposition of acrolein was found to yield: butylene, ethylene, carbon monoxide, methane, ethane and hydrogen. The kinetics of the reaction were complex.² The intermediacy of free radicals in the decomposition is suggested by the observation that the rate of consumption of acrolein at 470° was increased fourfold in the presence of ethylene oxide.³

More recently, di-*t*-butyl peroxide has been decomposed in acrolein vapor at both 134 and 169°.⁴ The products identified were *t*-butyl alcohol, acetone, ethane, methane and carbon monoxide. These substances, except for carbon monoxide, are typically obtained from the decomposition of the peroxide in a variety of media⁵ and thus provide no definite knowledge of the fate of the fragments derived from acrolein. The relatively high yields of carbon monoxide coupled with the small amounts of methane detected suggested that, at these temperatures, methyl radicals add to acrolein followed by polymerization of the aldehyde with the concerted loss of carbon monoxide at each propagation step.



From the approximate constancy of the sum of the yields of acetone and *t*-butyl alcohol it was concluded that *t*-butoxy fragments do not add readily to acrolein.

We wish to report some results obtained from a study of the thermal decomposition of acrolein in the gas phase. In conjunction with this investigation we have determined the pattern of attack of methyl and *t*-butoxy free radicals on acrolein.

Results and Discussion

The Thermal Decomposition of Acrolein.—Solutions of acrolein in toluene, benzene, cyclo-

(1) Department of Nematology, University of California, Riverside, Calif.

(2) H. W. Thompson and J. J. Frewing, *J. Chem. Soc.*, 1443 (1935).

(3) C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, **58**, 2135 (1936).

(4) D. H. Volman and R. K. Brinton, *J. Chem. Phys.*, **20**, 1764 (1952); D. H. Volman, *Trans. Faraday Soc. Disc.*, **14**, 253 (1953).

(5) J. H. Raley, F. F. Rust and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 88 (1945); **70**, 1336 (1945); E. R. Bell, F. F. Rust and W. E. Vaughan, *ibid.*, **72**, 337 (1950); F. F. Rust, F. H. Seibold and W. E. Vaughan, *ibid.*, **72**, 338 (1950).

pentane and butadiene were thermolyzed in a flow system. The results obtained in the first three diluents were essentially the same; thus only those in toluene at 600° and benzene at 500° are reported in detail (Tables I and II). Although the general features of the butadiene-acrolein pyrolysis were similar to the others, the extreme complexity of the pyrolysate discouraged a quantitative analysis of its constituents.⁶

TABLE I

PRODUCTS OF THE DECOMPOSITION OF ACROLEIN IN TOLUENE AT 600°

Mole ratio acrolein/toluene = 2.00; contact time, 4 sec. at 600°/1 atm.

Moles reacted ^a	Run A	Run B
Acrolein	1.43	1.45
Toluene	0.19	0.067
% conversion of acrolein	41	47
Products	Yield, ^b %	
Carbon monoxide	86	97
Ethylene	22	24
Propylene	9.2	8.7
Hydrogen	7.2	8.3
Methane	5.4	6.2
Ethane	4.4	3.3
1,3-Butadiene	3.4	3.4
1-Butene	3.0	2.3

^a Based on recovered starting material; more charring occurred in run A than in run B, although this was slight.

^b 100 (moles product/moles acrolein reacted).

TABLE II

MAJOR PRODUCTS OF THE DECOMPOSITION OF ACROLEIN IN BENZENE^a AT 500°

Mole ratio acrolein/benzene = 2.00; contact time, 9.8 sec. at 500°/1 atm.

Acrolein	Mole reacted		
Acrolein	0.41 (15.2% conv.)		
Benzene	0.016		
Products	Yield, %	Products	Yield, %
Carbon monoxide	100	1-Butene	3
Ethylene	20	1,3-Butadiene	2
Propylene	12	Methane	2
Ethane	3	Hydrogen	2
		Propane	2

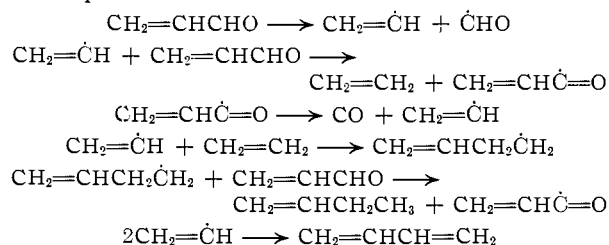
^a As was the case in toluene, small amounts of other substances were obtained, but these were not investigated.

In addition to those substances listed in Table I, the following were detected in the pyrolysate in amounts of 1% or less: acetylene, propyne, pro-

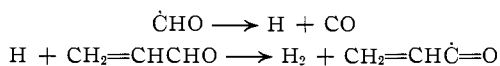
(6) A fraction of the product having b.p. 31–47° was found to contain 18 components.

pane, *cis*- and *trans*-butene-2, *n*-butane, isoprene, C₆H₁₀, cyclohexene, dihydropyran, allylbenzene and a mixture of C₇-aldehydes.⁷ The major products obtained from the pyrolysis of acrolein in benzene are listed in Table II.

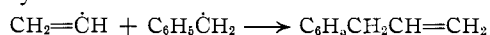
These results are partially interpreted in terms of a short chain decomposition of acrolein through vinyl radicals for which the acrylyl radical is a precursor. The initiation step is presumed to be that indicated by analogy with other aldehyde decompositions.⁸



At the higher temperature hydrogen atoms might also function as chain carriers.

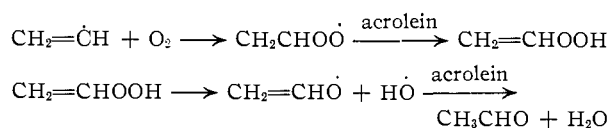


The suggested scheme of decomposition is consonant with the findings of recent studies of the photolysis of acrolein⁹ and is in accord with the results of the methyl radical induced decomposition of acrolein presented later. The presence of allylbenzene in the pyrolysate supports the intermediacy of vinyl radicals.¹⁰



Additional evidence for the free radical nature of the decomposition and for the participation of vinyl fragments was obtained by a cursory examination of the reaction in the presence of oxygen.

A 2:1 mixture of acrolein and air¹¹ thermolyzed at 500° for 10 sec. afforded no oxygenated derivatives of acrolein. All oxygen was consumed and no carbon dioxide was evolved. Under these conditions, which are identical to those of the acrolein-benzene pyrolysis, 84.2% of the aldehyde had dissipated. Moreover, along with the products typical of the decomposition in other media, the oxygen-catalyzed reaction led to the production of acet-aldehyde and water.



The majority of the trace quantities present in the acrolein pyrolysate are compatible with the proposed scheme of decomposition and can be ration-

(7) Cyclohexene-3-carboxaldehyde and others of uncertain structure.

(8) E. W. F. Steacie, "Atomic and Free Radical Reactions," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1954, pp. 206-219, and references therein.

(9) A. G. Harrison and F. P. Lossing, *Can. J. Chem.*, **1696** (1959); D. H. Volman, P. A. Leighton, F. E. Blacet and R. K. Brinton, *J. Chem. Phys.*, **18**, 205 (1950).

(10) No bibenzyl was found. The very small conversion of toluene indicates that hydrogen abstraction from acrolein is more rapid than from toluene.

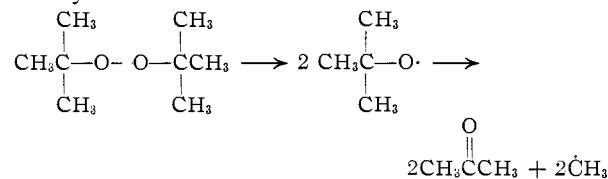
(11) Mole ratio acrolein/O₂ = 9.4.

alized in terms of well-known free radical pathways.¹² Clearly, the relatively high yields of propylene are not accommodated by the proposed mechanism, nor are the other odd-numbered carbon products. Moreover, the secondary decomposition of butene-1¹³ or ethylene¹⁴ cannot be invoked to explain these results, since these substances were not found to be appreciably decomposed, even under more drastic conditions than those of the acrolein thermolysis. Thus, at this time, it remains possible that other modes of decomposition of acrolein¹⁵ may be important at these temperatures, and that the above findings might also result from the decomposition of non-detected unstable intermediates.¹⁶

The Attack of Methyl Radicals on Acrolein.—Acrolein was subjected to an environment swamped with methyl radicals at 250° for 20 sec.¹⁷ (eleven half-lives of di-*t*-butyl peroxide) in a flow system. The results are presented in Table III.

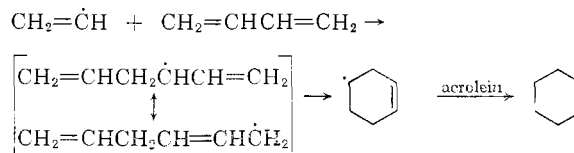
These data lend support to the suggested mechanism of decomposition of acrolein at higher temperatures, and they allow an estimation of the relative importance of methyl addition to acrolein as compared to hydrogen abstraction.

Methyl radicals result from decomposition of the peroxide.⁴ The higher temperature employed favors the collapse of *t*-butoxy to acetone and methyl.



The material balance for di-*t*-butyl peroxide taken from Table III is: di-*t*-butyl peroxide = 1/2 (acetone + *t*-butyl alcohol); found: 0.65 \cong 0.62. Thus it is valid that the number of moles of methyl radicals produced equals the number of moles of acetone detected.

(12) The cyclic olefins are interesting in that although they may result from a thermal Diels-Alder reaction (the high temperature is certainly unfavorable to this process; cf. F. O. Rice, P. M. Ruoff and E. L. Rodowskas, *J. Am. Chem. Soc.*, **60**, 955 (1938); they can also be rationalized as radical addition-cyclization products. Thus, cyclohexene might arise *via*



Cf. L. M. Porter and F. F. Rust, *J. Am. Chem. Soc.*, **78**, 5571 (1956).

(13) The thermal dissociation of butene-1 to methyl and allyl radicals has been reported; A. H. Schon and M. Szwarc, *Proc. Roy. Soc. (London)*, **A202**, 263 (1950); *J. Chem. Phys.*, **18**, 237 (1950).

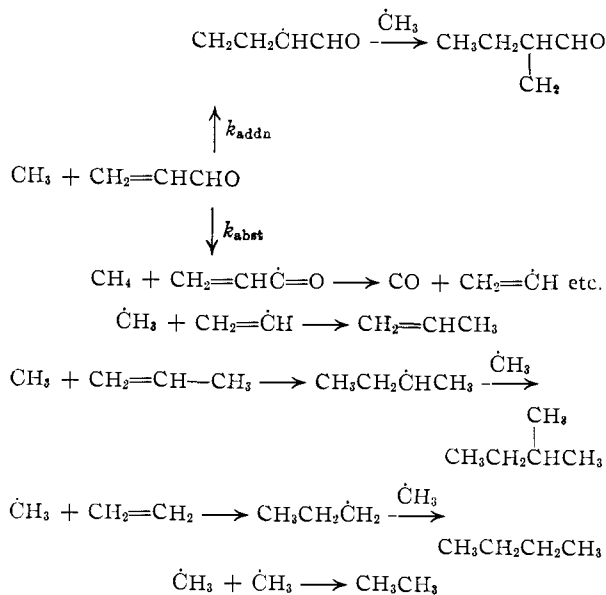
(14) For a review of the thermal decomposition and polymerization of ethylene, cf. ref. 8, pp. 175-183.

(15) For example, a direct dissociation of acrolein to methylene and carbon monoxide.

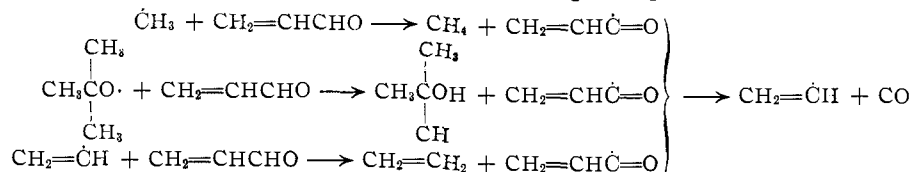
(16) The addition of vinyl radicals to acrolein should yield ω -pentalen which might be expected to cleave to allyl and formylmethyl radicals in a manner analogous to the cleavage of 1,5-hexadiene; W. A. Bryce and D. J. Ruzicka, *Can. J. Chem.*, **38**, 835 (1960); and unpublished results of the authors.

(17) At temperatures below 400° the decomposition of acrolein is slow. The pure aldehyde at 350° for 1.6 min. remained intact. At 180° for one half-life of di-*t*-butyl peroxide (5%) only small amounts of disacryl polymer were found.

Methyl radicals are consumed by the paths

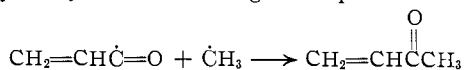


If the most prevalent radicals in the system abstract hydrogen from acrolein, and if the resulting acrylyl fragment rapidly decomposes

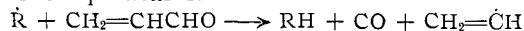


then $\text{CO} = \text{CH}_4 + \text{CH}_2 = \text{CH}_2 + t\text{-BuOH}$; found: $0.068 \pm 0.004 = 0.060 + 0.0075 + 0.012 = 0.079$, or using the upper limit for CO: $0.072 \cong 0.079$. The agreement is within the experimental error.¹⁸

These results confirm the short chain decomposition of acrolein through vinyl radicals and they attest to the instability of acrylyl noted above. This instability is further manifested in the lack of methyl vinyl ketone amongst the products.



In fact, loss of carbon monoxide from acrolein may occur concomitantly with hydrogen abstraction at these temperatures.



The relative importance of addition to acrolein and hydrogen abstraction from the aldehyde by methyl radicals may be estimated from the expression

$$\frac{k_{\text{addn}}}{k_{\text{abst}}} \cong \frac{\text{CH}_3\overset{\text{O}}{\parallel}{\text{C}}\text{CH}_3 - (\text{CH}_4 + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CHO} + \text{CH}_2=\text{CHCH}_3 + 3\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)_2 + 2\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_2\text{CH}_2\text{CH}_3 + 2\text{C}_2\text{H}_6)}{\text{CH}_4}$$

Employing the data of Table III, $k_{\text{addn}}/k_{\text{abst}} \cong 4$. Thus, at 250° methyl radicals predominantly add to acrolein, as Volman and Brinton observed at lower temperatures.⁴

(18) The relative error in yield of all products being approximately $\pm 6\%$.

TABLE III

PRODUCTS FROM THE METHYL RADICAL INDUCED DECOMPOSITION OF ACRYLEIN AT 250°

Charged: di-*t*-butyl peroxide, 0.646 mole; acrolein, 1.93 moles; contact time, 20 sec. at 250°/1 atm.; moles acrolein reacted, 0.258, ^a 13.4% conversion.

Products	Moles
Acetone	1.23
Ethane	0.39
2-Methylbutyraldehyde	.096
Carbon monoxide	.068 \pm 0.004
Methane	.060
Propylene	.016
<i>t</i> -Butyl alcohol	.012
1-Butene	.011
Ethylene	.0075
Isopentane	.0043
2,3-Dihydro-4H-pyranyl-2-carboxaldehyde	.0033
Propane	.0017
1,3-Butadiene	.0010
<i>n</i> -Butane	.0006
2-Butene	.0005

^a The weight of acrolein not accounted for by the listed products is 4.5 g. From the pyrolysate there was obtained a heavy non-distillable oil and a very high boiling fraction (presumably low mol. wt. polymers of acrolein which contained only a small number of carbonyl groupings) together amounting to 5.3 g.

The Attack of *t*-Butoxy Radicals on Acrolein.—Although evidence for the transient existence of acrylyl fragments in the gas phase decompositions of acrolein at higher temperatures seems quite compelling, no products of these decompositions could be detected that might be considered to directly result from an acrylyl precursor. The elusive nature of these species in the gas phase suggested that they might be captured at low temperatures in solution. The problem is compounded, however, by the easy polymerization of acrolein.¹⁹ In light of the propensity of *t*-butoxy radicals for allylic hydrogen abstractions²⁰ and the effectiveness of *t*-butyl hypochlorite²¹ as a chlorine transfer agent, it was hoped that the hypohalite might provide a vehicle for both generating and trapping acrylyls²² in solution.

This expectation was fully confirmed by examining the photolysis of a dilute solution of acro-

(19) Thus, in our hands, both the succinimidyl and benzyloxy radicals rapidly polymerized dilute solutions of acrolein.

(20) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957. Chapter 10, and references therein.

(21) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108, 6113 (1960).

(22) The conversion of benzaldehyde to benzoyl chloride by *t*-butyl hypochlorite has been noted; D. Ginsburg, *ibid.*, **73**, 702 (1951).

glycol column resolved carbon tetrachloride, *t*-butyl alcohol and *t*-butyl acrylate from a mixture of acrolein and acetone. The acrolein-acetone pair was resolved on β,β' -oxydipropionitrile. The blip corresponding to *t*-butyl acrylate was trapped ten times from the triethylene glycol column. Its infrared spectrum was identical with the spectrum of authentic gaseous *t*-butyl acrylate.²⁸

Acknowledgment.—The authors are indebted to Mr. F. L. Rodgers for patient assistance with the experimentation.

(28) This substance was prepared in poor yield from acrylyl chloride and *t*-butyl alcohol in the presence of Na_2CO_3 ; b.p. 56° (80 mm.), n_D^{20} 1.4102.

[CONTRIBUTION FROM THE DOW CORNING CORPORATION, MIDLAND, MICH.]

The Effect of Polar Substituents on the Acid-catalyzed Hydrolysis of Organosilicon Hydrides

BY OMAR W. STEWARD AND OGDEN R. PIERCE

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The first-order rate constants for the acid-catalyzed hydrolysis of sixteen fluoroalkyl-, ω -cyanoalkyl- and *n*-alkylsilicon hydrides have been determined using aqueous ethanolic hydrochloric acid (1.43 *N*, 95 vol.-% ethanol) at 34.8° . The first-order rate constants are correlated using the Taft equation. The correlations are discussed in terms of polar effects, steric effects and dative π -bonding.

Introduction

The polar effect of substituted alkyl groups on the alkali-catalyzed hydrolysis of triorganosilicon hydrides has been reported previously.¹ An excellent correlation of the second-order rate constants was obtained using the Taft equation² for triorganosilicon hydrides containing fluoroalkyl, ω -cyanoalkyl and *n*-alkyl groups.^{1a}

Other linear relationships involving the inductive effect of substituent groups in silicon hydrides have been reported: (a) Hammett's σ -values and modified σ -values *vs.* $\log k$ for the base-catalyzed hydrolysis of triorganosilanes,³ (b) ν SiH (cm.⁻¹) *vs.* empirically determined *E*-values and Taft's σ^* -values,⁴ (c) ν SiH (cm.⁻¹) *vs.* τ (p.p.m.) for a proton attached to silicon,⁵ (d) ν SiH (cm.⁻¹) *vs.* $\log K$ (25°) for the hydrolysis of triorganochlorosilanes.⁶

The acid-catalyzed solvolysis of organosilicon hydrides has been studied by Taketa, *et al.*,⁷ and Baines and Eaborn.⁸ In this paper a study is reported on the effect of polar substituents on the acid-catalyzed hydrolysis of mono-, di- and triorganosilicon hydrides. The first-order rate constants are correlated using the Taft equation. The correlations are discussed in terms of polar effects, steric effects and dative π -bonding.

Experimental

Starting Materials.—Trichlorosilane, 3,3,3-trifluoropropyltrichlorosilane,⁹ β -trichlorosilylpropionitrile,^{10,11} β -methyl-

dichlorosilylpropionitrile,^{10,11} chloromethyl dimethylchlorosilane¹² and 3-bromo-1,1,1-trifluoropropane¹³ were available in research quantities. They were fractionally distilled before being used.

Preparation of 3,3,3-Trifluoropropyl-*n*-butyldiethoxysilane and Bis-(3,3,3-trifluoropropyl)-diethoxysilane.—Absolute ethanol (194 g., 4.2 moles) was added to 3,3,3-trifluoropropyltrichlorosilane (463 g., 2.0 moles) over a period of 0.5 hour. Throughout the addition the reaction temperature was maintained between 50 – 60° . After addition was complete, the mixture was heated to 120° and allowed to cool to room temperature. The reaction mixture was then stirred for 16 hours with a slow nitrogen sweep to remove any remaining hydrogen chloride. The material in the flask, 3,3,3-trifluoropropylethoxychlorosilanes (493 g.), analyzed for one chlorine per silicon, a 98% yield.

Anal. Calcd. for $\text{C}_7\text{H}_{13}\text{ClF}_3\text{O}_2\text{Si}$: Cl, 14.15. Found: Cl, 14.4.

n-Butylmagnesium bromide, dissolved in ether (550 ml.), prepared from *n*-butyl bromide (116 g., 0.85 mole) and magnesium (20.7 g., 0.85 mole), was added to the above prepared 3,3,3-trifluoropropylethoxychlorosilanes (213 g., 0.85 mole), dissolved in ether (200 ml.), over a period of 0.5 hour. Throughout the addition the reaction mixture was cooled in an ice-bath. After refluxing for 16 hours, the reaction mixture was poured onto a mixture of cracked ice and sodium bicarbonate (212 g., 2.0 moles). The ether layer was washed and dried over anhydrous calcium sulfate. After removing the ether, fractional distillation gave: 3,3,3-trifluoropropyltriethoxysilane¹⁴ (33.5 g., 0.13 mole), b.p. 82° (30 mm.), n_D^{25} 1.3650, a 15% yield; 3,3,3-trifluoropropyl-*n*-butyldiethoxysilane (146 g., 0.54 mole), b.p. 105° (30 mm.), n_D^{25} 1.3858, d_4^{25} 0.991, a 63% yield.

Anal. Calcd. for $\text{C}_{11}\text{H}_{23}\text{F}_3\text{O}_2\text{Si}$: C, 48.5; H, 8.51; F, 20.9. Found: C, 49.0; H, 8.65; F, 21.1.

3,3,3-Trifluoropropyl-*n*-butylethoxysilane (5.3 g., 0.019 mole), b.p. 126.5° (30 mm.), n_D^{25} 1.4073, d_4^{25} 0.944, a 2% yield.

Anal. Calcd. for $\text{C}_{15}\text{H}_{27}\text{F}_3\text{O}_2\text{Si}$: C, 54.9; H, 9.57; F, 20.0. Found: C, 55.8; H, 10.1; F, 19.9.

Using the same procedure described above, 3,3,3-trifluoropropylmagnesium bromide, dissolved in ether (500 ml.), prepared from 3-bromo-1,1,1-trifluoropropane (150 g., 0.85 mole) and magnesium (20.7 g., 0.85 mole), was added to the 3,3,3-trifluoropropylethoxychlorosilanes (213 g., 0.85 mole). Fractional distillation gave: 3,3,3-trifluoropropyltriethoxysilane¹⁴ (15.4 g., 0.06 mole), b.p.

(10) J. C. Saam and J. L. Speier, *J. Org. Chem.*, **24**, 427 (1959).

(11) G. D. Cooper and M. Prober, *ibid.*, **25**, 240 (1960).

(12) R. H. Krieble and J. R. Elliott, *J. Am. Chem. Soc.*, **67**, 1810 (1945).

(13) P. Tarrant, A. M. Lovelace and M. R. Lilyquist, *ibid.*, **77**, 2783 (1955).

(14) O. W. Steward and O. R. Pierce, *J. Org. Chem.*, **26**, 2943 (1961).

(1) (a) O. W. Steward and O. R. Pierce, *J. Am. Chem. Soc.*, **83**, 1916 (1961); (b) **81**, 1983 (1959).

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(6) J. F. Hyde, P. L. Brown and A. L. Smith, *J. Am. Chem. Soc.*, **82**, 5854 (1960).

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(9) P. Tarrant, G. W. Dyckes, R. Dunmire and G. B. Butler, *J. Am. Chem. Soc.*, **79**, 6536 (1957).