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Vinyl Derivatives of Metals. XIII. Some Addition Reactions of Triethylperfluorovinylsilane. The F^{19} Nuclear Resonance Spectra of the Triethylperfluorovinyl Derivatives of Silicon, Germanium, and Tin and of Perfluorovinyltriethoxysilane[1]

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The reactions of triethylperfluorovinylsilane with bromine, hydrogen bromide, bromotrichloromethane, carbon tetrabromide, and trifluoroiodomethane result in $(C_2H_5)_3SiCFBrCF_2Br$, $(C_2H_5)_3SiCFHCF_2Br$, $(C_2H_5)_3SiCFBrCF_2CCl_3$, $(C_2H_5)_3SiCFBrCF_2CBr_3$, and $(C_2H_5)_3SiCFICF_2CF_3$, respectively. The structures of the hydrogen bromide and bromotrichloromethane adducts were confirmed using n.m.r. spectroscopy. Chlorine does not add across the double bond, but chlorinates ethyl groups instead. The preparations of perfluorovinyltriethoxysilane, triethylperfluorovinylgermane, and triphenylperfluorovinylgermane are described.

The reaction of vinylsilicon compounds with electrophilic and radical reagents has received extensive study.[2] The availability of triethylperfluorovinylsilane[1,3] has made possible a comparison of its reactions with such reagents with the analogous reactions of triethylvinylsilane. The present brief investigation of the reactions of the halogens, the hydrogen halides, and polyhalomethanes with triethylperfluorovinylsilane has demonstrated that substitution of all three hydrogen atoms of the vinyl group in vinylsilanes by fluorine results in a markedly diminished reactivity toward these reagents.

Trialkylvinylsilanes react readily with chlorine and bromine at low temperature, giving α,β-dihaloethyltrialkylsilanes.[2] Triethylperfluorovinylsilane also underwent bromine addition to give $(C_2H_5)_3SiCFBrCF_2Br$, but at a much slower rate. An experiment in which equimolar quantities of triethylvinylsilane and triethylperfluorovinylsilane were allowed to compete for one equivalent of bromine confirmed this qualitative observation. The bromine adduct of triethylperfluorovinylsilane could be debrominated in good yield with zinc in tetrahydrofuran. This bromination–debromination sequence has proved useful in the synthesis of compounds whose separation by distillation from excess of starting material or from the solvent was difficult to realize with the equipment available to us. Thus perfluorovinyltriethoxysilane, prepared in low yield by the reaction of perfluorovinylmagnesium bromide with tetraethoxysilane, was separated from unreacted tetraethoxysilane by bromination to $(C_2H_5O)_3SiCFBrCF_2Br$, whose isolation by distillation was effected easily. This bromine adduct then was debrominated in 66% yield to give pure perfluorovinyltriethoxysilane. A similar separation of trimethylperfluorovinylsilane from the tetrahydrofuran solvent used in the perfluorovinylation reaction was of preparative utility.[4]

Chlorination of triethylperfluorovinylsilane, on the other hand, did not result in the expected addition reaction. Instead, chlorination of ethyl groups seemed to occur when triethylperfluorovinylsilane was treated with chlorine in carbon tetrachloride at 0°. Similar resistance to chlorine addition has been described in the case of trimethylperchlorovinylsilane.[5] Attempted addition of iodine to triethylperfluorovinylsilane in a sealed tube at 100° during one week was unsuccessful. It may be noted that tetrafluoroethylene will undergo iodine addition under mild conditions.[6]

Triethylperfluorovinylsilane reacted with hydrogen bromide in the presence of benzoyl peroxide at $-20°$ to give $(C_2H_5)_3SiCFHCF_2Br$. The structure of this product was shown to be

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[1] Part XII: D. Seyferth and R. H. Towe, *Inorg. Chem.*, **1**, 185 (1962).

[2] For a review see: D. Seyferth, "Vinyl Compounds of Metals" in "Progress in Inorganic Chemistry," Vol. III (F. A. Cotton, editor), Interscience Publishers Inc., New York, N. Y., 1962 (in press).

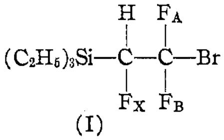
[3] D. Seyferth, K. A. Brändle, and G. Raab, *Angew. Chem.*, **72**, 77 (1960).

[4] D. Seyferth and D. E. Welch, unpublished results.

[5] E. T. McBee, C. W. Roberts, and G. W. R. Puerckhauer, *J. Am. Chem. Soc.*, **79**, 2326 (1957).

[6] H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 2948 (1949).

that written by analysis of its F^{19} nuclear resonance spectrum. The n.m.r. spectrum, obtained at 40 Mc./sec., contained 22 lines due to F^{19} resonance. A low field group (AB) of 14 lines was centered at 464 ± 2.5 c.p.s. at lower field than the benzotrifluoride reference line, while an eight-line group was centered at 6240 ± 52 c.p.s. at higher field than the reference line. Since the spin couplings between the three fluorine nuclei and the ethane proton were found to be extremely small compared to the chemical shifts between them, $|\nu_F - \nu_H / J_{FH}| >> 1$, the influence of the proton on the spectrum was considered a first order effect. Consequently, the adduct was treated initially as an ABX system, and the effects of the proton–fluorine splittings were superimposed on the result. This treatment predicted line positions and intensities in good agreement with the observed spectrum when the following parameters were employed[7]: $\nu_A - \nu_A = 256 \pm 2.5$ c.p.s.; $|J_{AB}| = 168 \pm 2.5$ c.p.s.; $|J_{BX}| = 33.0 \pm 0.4$ c.p.s.; $|J_{AX}| = 22.0 \pm 0.3$ c.p.s.; $|J_{AH}| = 22.0 \pm 0.3$ c.p.s.; $|J_{BH}| = 10.0 \pm 0.3$ c.p.s.; $|J_{XH}| = 43.5 \pm 0.6$ c.p.s. On the basis of the data available in similar systems,[8–11] these values are readily accounted for in terms of the assumed structure for the adduct (I).



$$(C_2H_5)_3Si-\overset{\overset{H}{|}}{\underset{\underset{F_X}{|}}{C}}-\overset{\overset{F_A}{|}}{\underset{\underset{F_B}{|}}{C}}-Br$$

(I)

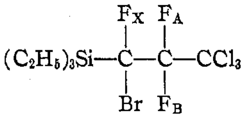
Anhydrous hydrogen iodide in the absence of a catalyst reacted with triethylperfluorovinylsilane to give a low yield of a liquid, b.p. 55–56° at 0.45 mm., $n^{25}D$ 1.4586, assumed to be $(C_2H_5)_3SiCFHCF_2I$. This initially light yellow product, however, was quite unstable, becoming dark red within a few hours, and an analysis was not obtained. Anhydrous hydrogen chloride did not appear to react with triethylperfluorovinylsilane under conditions reported[12] for the successful hydrochlorination of triethylvinylsilane.

Radical-initiated additions of polyhalomethanes to triethylperfluorovinylsilane were successful only when the more active bromotrichloromethane, carbon tetrabromide, and trifluoroiodomethane were used

$$(C_2H_5)_3Si-CF{=}CF_2 + BrCX_3 \xrightarrow[\text{peroxide}]{\text{benzoyl}} (C_2H_5)_3SiCFBrCF_2CX_3 \ (X = \text{Cl and Br})$$

The adduct formed with trifluoroiodomethane, presumably $(C_2H_5)_3SiCFICF_2CF_3$, also decomposed quite rapidly, becoming dark red, and an analysis was not possible. Carbon tetrachloride and chloroform did not appear to react with the perfluorovinylsilane under the same conditions. In contrast, addition of these reagents to trialkylvinylsilanes proceeded quite readily in the presence of benzoyl peroxide.[2]

An n.m.r. analysis of the bromotrichloromethane adduct yielded an eleven-line F^{19} spectrum upon examination at 40 Mc./sec. The high field lines (X), forming a 1:2:1 triplet, were separated from the internal reference line of benzotrifluoride by 3260 ± 11 c.p.s., while an eight-line pattern (AB) was centered 1240 ± 9 c.p.s. at higher field than the reference line. When the adduct was treated as an ABX system,[13] predicted line positions and intensities were obtained in good agreement with the observed spectrum by employing the parameters: $\nu_A - \nu_B = 96.6 \pm 2.8$ c.p.s.; $|J_{AB}| = 253 \pm 2.8$ c.p.s.; $|J_{AX}| = 13.6 \pm 0.2$ c.p.s.; $|J_{BX}| = 11.2 \pm 0.2$ c.p.s. In light of similar data available for substituted 1,1,2-trifluoroethanes,[8–11] these parameters are entirely consistent with the proposed structure of the adduct (II).



$$(C_2H_5)_3Si-\overset{\overset{F_X}{|}}{\underset{\underset{Br}{|}}{C}}-\overset{\overset{F_A}{|}}{\underset{\underset{F_B}{|}}{C}}-CCl_3$$

(II)

The availability of triethyl- and triethoxyperfluorovinylsilane, of triethylperfluorovinyltin from previous work,[3] and of the new triethylperfluorovinylgermane (see Experimental section) made possible a study of their F^{19} n.m.r. spectra; the results obtained are summarized here. The fluorine nuclear magnetic resonance spectra of these four compounds (obtained at 40 Mc./sec.) in each case consisted of three widely separated quartets, each corresponding to one of the three

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(7) The detailed presentation, analysis, and discussion of the F^{19} nuclear resonance spectra of this compound and of other saturated and unsaturated 1,1,2-trifluoro compounds will be reported elsewhere by G. E. M.

(8) L. M. Crapo and C. H. Sederholm, *J. Chem. Phys.*, **33**, 1583 (1960).

(9) L. Petrakis and C. H. Sederholm, *ibid.*, in press.

(10) J. Lee and L. H. Sutcliffe, *Trans. Faraday Soc.*, **54**, 308 (1958).

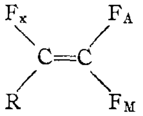
(11) J. J. Drysdale and W. D. Phillips, *J. Am. Chem. Soc.*, **79**, 319 (1957).

(12) E. Larsson, *Chalmers Tek. Högskol. Handl.*, No. **115**, 25 (1951); *Chem. Abstr.*, **47**, 10470 (1953).

(13) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, New York, N. Y., 1959.

TABLE I

SUMMARY OF N.M.R. PARAMETERS FOR

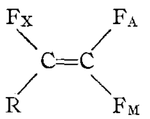


R	Chemical Shifts, p.p.m. from $C_6H_5CF_3$[a]			Coupling Constants, c.p.s.		
	δ_A	δ_M	δ_X	$\lvert J_{AM}\rvert$[b]	$\lvert J_{AX}\rvert$[c]	$\lvert J_{MX}\rvert$[d]
$(C_2H_5O)_3Si$	23.5 ± 0.2	50.3 ± 0.3	139.8 ± 0.5	59.3 ± 0.5	24.9 ± 0.6	117.4 ± 0.9
$(C_2H_5)_3Si$	24.3 ± 0.2	53.7 ± 0.5	135.1 ± 0.4	70.5 ± 1.1	26.5 ± 0.9	115.1 ± 1.2
$(C_2H_5)_3Ge$	26.4 ± 0.2	58.3 ± 0.4	130.8 ± 0.6	78.8 ± 0.9	31.9 ± 0.7	115.5 ± 1.0
$(C_2H_5)_3Sn$	25.6 ± 0.2	60.6 ± 0.3	130.1 ± 0.6	80.7 ± 1.1	33.7 ± 0.6	113.7 ± 0.7

[a] Internal reference (R), $\delta_A = \frac{H_A - H_R}{H_R} \times 10^6$. [b] $J_{AM} = J_{gem}$. [c] $J_{AX} = J_{cis}$. [d] $J_{MX} = J_{trans}$.

non-equivalent fluorine nucleii, from which the spin coupling constants were obtained directly on the basis of line separations. Since the ratio of spin-coupling constant to chemical shift for any pair of nuclei is quite small in these molecules, these three-spin arrangements may be considered simple examples of AMX systems.

In each case the three multiplets occurred at approximately 1000 c.p.s. (A), 2000 c.p.s. (M), and 5300 c.p.s. (X) higher field than the reference line of benzotrifluoride. Since the environments of the two *gem* fluorine nuclei should be similar and quite distinct from that of the remaining fluorine nucleus, the two low-field quartets (A and M), lying relatively close together, were assigned to the $=CF_2$ group. The structural distinction between the *gem* fluorines (A and M) was made on the basis of spin-coupling constants. In all the fluoroölefins so far studied[14,15] the spin-coupling constant between two fluorine nuclei located *trans* to each other is approximately 110–120 c.p.s., considerably greater than the couplings between *cis* or between *gem* fluorines. Therefore, the low field quartets exhibiting a splitting constant of about 115 c.p.s. were considered to arise from the fluorine nucleus *trans* to the fluorine on the carbon atom bearing the organometallic substituent. In every case these large splittings occurred in the M multiplet. Thus the following assignment was made



R = $(C_2H_5O)_3Si$, $(C_2H_5)_3Si$, $(C_2H_5)_3Ge$, and $(C_2H_5)_3Sn$

The n.m.r. results are summarized in Table I. Inspection of Table I reveals that in each case $\delta_A < \delta_M < \delta_X$ and $J_{trans} > J_{gem} > J_{cis}$, the same trends which have been observed in previous n.m.r. investigations of other perfluorovinyl compounds.[14,15] Currently in progress are additional n.m.r. studies of other perfluorovinyl compounds, aimed at determining the extent and nature of the correlation between the three coupling constants and the type of substituent (R) in $CF_2{=}CFR$.

Experimental[16]

Bromination of Triethylperfluorovinylsilane.—To a solution of 7.3 g. (0.037 mole) of triethylperfluorovinylsilane in 90 ml. carbon tetrachloride at 0° was added during 5 hr. 5.9 g. (0.037 mole) of bromine in 15 ml. carbon tetrachloride. The resulting yellow solution was distilled to give 1.4 g. of triethylperfluorovinylsilane and 10 g. (75%) of $(C_2H_5)_3SiCFBrCF_2Br$, b.p. 62° (0.72 mm.), $n^{25}D$ 1.4672.

Anal. Calcd. for $C_8H_{15}F_3Br_2Si$: C, 26.98; H, 4.25; Br, 44.87. Found: C, 27.20; H, 4.53; Br, 44.83. Debromination of the product with zinc in tetrahydrofuran gave triethylperfluorovinylsilane in 66% yield.

Competitive Bromination of Triethylperfluorovinylsilane and Triethylvinylsilane.—A mixture of 7.0 g. (0.036 mole) of triethylperfluorovinylsilane and 5.2 g. (0.036 mole) of triethylvinylsilane in 110 ml. of carbon tetrachloride was treated with 0.036 mole of bromine at 0°. Trace amounts of fuming substances made fractional distillation of the resulting solution difficult. The following fractions were obtained: (1) $(C_2H_5)_3SiCF{=}CF_2$, b.p. 34.5–34.8° (10 mm.), 4.44 g. (63%); (2) $(C_2H_5)_3SiCH{=}CH_2$, b.p. 43.5–44° (11 mm.), 1.10 g. (21%); (3) $(C_2H_5)_3SiCFBrCF_2Br$, b.p. 65.5–66.5° (0.65 mm.), 4.59 g. (36%); (4) $(C_2H_5)_3SiCHBrCH_2Br$, b.p. 82° (0.6 mm.), 6.33 g. (58%).

Preparation of Triethoxyperfluorovinylsilane.—A solution of 47.9 g. (0.296 mole) of bromotrifluoroethylene (Peninsular ChemResearch, Inc.) and 50 g. (0.240 mole) of tetraethoxysilane in 170 ml. tetrahydrofuran (THF) was added dropwise to 7.2 g. (0.295 g. atom) of activated magnesium turnings in 50 ml. THF at −20°. The reaction mixture was stirred under nitrogen for 8 hr. at 0° to −3°, and then was filtered. The filtrate was distilled to give a fraction of b.p. 55° (9.5 mm.), which, according to its infrared spectrum, consisted of tetraethoxysilane and a

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(14) H. M. McConnell, C. A. Reilly, and A. D. McLean, *J. Chem. Phys.*, **24**, 479 (1956).

(15) J. D. Swalen and C. A. Reilly, *ibid.*, **34**, 2122 (1961).

(16) Analyses by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

small amount of a $CF_2{=}CFSi$ compound. This fraction was treated with 10 g. of bromine in 30 ml. of carbon tetrachloride at 0° during three days. Fractional distillation gave, in addition to tetraethoxysilane, 7.5 g. (8%) of a pale yellow liquid, b.p. 63–64° (0.25 mm.), $n^{25}D$ 1.4212, presumably impure $(C_2H_5O)_3SiCFBrCF_2Br$.

Anal. Calcd. for $C_8H_{15}O_3F_3Br_2Si$: C, 23.78; H, 3.74; Br, 39.04. Found: C, 25.33; H, 4.49; Br, 37.34.

To 7.0 g. (0.017 mole) of this product in 20 ml. THF was added 1.5 g. (0.023 g.-atom) of zinc powder, and the mixture was stirred for 30 min. The exothermic reaction which took place was moderated by external cooling. Distillation of the reaction mixture gave 2.8 g. (66%) of triethoxyperfluorovinylsilane, b.p. 40° (10 mm.), $n^{25}D$ 1.3678.

Anal. Calcd. for $C_8H_{15}O_3F_3Si$: C, 39.33; H, 6.19; F, 23.33. Found: C, 39.18; H, 6.26; F, 23.08.

Chlorination of Triethylperfluorovinylsilane.—To 5.9 g. (0.03 mole) of triethylperfluorovinylsilane in 30 ml. carbon tetrachloride at 0° was added dropwise 2.2 g. (0.03 mole) of chlorine dissolved in 30 ml. carbon tetrachloride. Unreacted chlorine and solvent were removed at reduced pressure after 3 hr. Fractional distillation of the residue gave 2.5 g. (42% recovery) of triethylperfluorovinylsilane, 2.8 g. of pale yellow liquid, b.p. 48–51° (1.4 mm.), and 1.8 g. of pale yellow liquid, boiling range 60–90° (1.4 mm.), $n^{25}D$ 1.4634. The 48–51° fraction was redistilled (mainly at 50° at 1.5 mm.) to give material, $n^{25}D$ 1.4340, whose analysis agreed fairly well with that calculated for $(C_2H_5)_2(C_2H_4Cl)SiCF{=}CF_2$. Its infrared spectrum showed strong absorption due to the $CF{=}CF_2$ group.

Anal. Calcd. for $C_8H_{14}F_3ClSi$: C, 41.64; H, 6.12. Found: C, 41.04; H, 6.26.

Hydrobromination of Triethylperfluorovinylsilane.—Hydrogen bromide gas was bubbled through a trap containing 9.5 g. (0.048 mole) of triethylperfluorovinylsilane and 0.1 g. of benzoyl peroxide at −20° during 2.5 hr. Distillation of the reaction mixture gave 6.0 g. of unreacted triethylperfluorovinylsilane and 3.1 g. of the adduct, $(C_2H_5)_3SiCHFCF_2Br$, b.p. 43.5° (0.92 mm.), $n^{25}D$ 1.4358, a colorless liquid. *Anal.* Calcd. for $C_8H_{16}F_3BrSi$: C, 34.64; H, 5.82; Br, 28.84. Found: C, 34.91; H, 5.71; Br, 28.96.

Reaction of Triethylperfluorovinylsilane with Bromotrichloromethane.—A mixture of 5.9 g. (0.03 mole) of triethylperfluorovinylsilane and 6 g. of bromotrichloromethane was heated to 90°, and a solution of 0.5 g. of benzoyl peroxide in 11 g. of bromotrichloromethane was added slowly in small portions with rapid stirring. The temperature was maintained at 100° during the addition, and the reaction mixture was heated subsequently at 115° for 4.5 hr. Fractional distillation gave a 44% recovery of triethylperfluorovinylsilane (2.6 g.) and 5.4 g. (45.5%) of $(C_2H_5)_3SiCFBrCF_2CCl_3$, b.p. 96.5° (0.8 mm.), $n^{25}D$ 1.4838.

Anal. Calcd. for $C_9H_{15}F_3Cl_3BrSi$: C, 27.40; H, 3.83; Cl, 26.99; Br, 20.76. Found: C, 27.55; H, 3.86; Cl, 26.82; Br, 20.42.

Reaction of Triethylperfluorovinylsilane with Carbon Tetrabromide.—To 20 g. (0.06 mole) of carbon tetrabromide at 90° was added dropwise 5.9 g. (0.03 mole) of triethylperfluorovinylsilane containing 0.3 g. of di-*t*-butyl peroxide. The reaction mixture was heated at 130–135° for 1.5 hr. under nitrogen. Fractional distillation gave 8.5 g., b.p. 50–53° (28–30 mm.); 4.0 g., boiling range 93° (20 mm.) to 114° (5.0 mm.); 9.1 g. (58%), b.p. 133–138° (0.2 mm.). The last fraction was redistilled to give pure $(C_2H_5)_3SiCFBrCF_2CBr_3$, b.p. 134–135° (0.15 mm.), $n^{25}D$ 1.5463.

Anal. Calcd. for $C_9H_{15}F_3Br_4Si$: C, 20.47; H, 2.87; F, 10.80; Br, 64.34. Found: C, 20.20; H, 2.67; F, 10.61; Br, 64.07.

Reaction of Triethylperfluorovinylsilane with Trifluoroiodomethane.—A mixture of 4.0 g. each of triethylperfluorovinylsilane and trifluoroiodomethane and 0.2 g. of di-*t*-butyl peroxide was heated for 1.5 hr. at 125–130° in a nitrogen-filled, sealed, heavy-walled Pyrex tube. Distillation of the reaction mixture resulted in recovery of 1.3 g. of triethylperfluorovinylsilane and in isolation of a fraction, b.p. 63–64° (1.5 mm.), $n^{25}D$ 1.4583, 2.2 g., which may have been the desired $(C_2H_5)_3SiCFICF_2CF_3$. The initially colorless distillate, however, changed to pink and then to red fairly rapidly, and for this reason an analysis was not obtained.

Preparation of Triethyl- and Triphenylperfluorovinylgermane.—A mixture of 30 g. (0.104 mole) of triethyliodogermane and 24 g. of bromotrifluoroethylene in 200 ml. tetrahydrofuran was added to 3.6 g. (0.148 g.-atom) of magnesium in 100 ml. tetrahydrofuran, using the conditions and procedure described in detail for the preparation of triethylperfluorovinylsilane.[1] Triethylperfluorovinylgermane, b.p. 45° (10 mm.), $n^{25}D$ 1.4138, was obtained in 40% yield.

Anal. Calcd. for $C_8H_{15}F_3Ge$: C, 39.90; H, 6.28; F, 23.67. Found: C, 39.35; H, 6.12; F, 23.55.

A similar procedure was used in the reaction of 9.5 g. (0.025 mole) of triphenylbromogermane, 19 g. (0.118 mole) of bromotrifluoroethylene, and 0.12 g.-atom of magnesium. The sticky brown residue from the organic layer after hydrolysis was extracted with ethanol and the extracts passed through an alumina column and evaporated. The residue was recrystallized from hexane to give 3 g. (31.3%) of triphenylperfluorovinylgermane, m.p. 84°.

Anal. Calcd. for $C_{20}H_{15}F_3Ge$: C, 62.40; H, 3.99; F, 14.81. Found: C, 62.18; H, 4.20; F, 14.51.

N.m.r. Spectra.–The n.m.r. spectra were obtained with a standard 40 Mc./sec. high-resolution spectrometer from Varian Associates (V4300B, equipped with a superstabilizer and a field homogeneity control unit). Line positions and separations were measured using the sideband technique.[13] In order to minimize the effects of instrument instabilities, especially magnetic field drift, each sidebanded spectrum was obtained at least ten times; thus, line positions have been averaged over at least ten measurements in each case. The limits of precision indicated in the work represent average deviations in these repeated measurements. The n.m.r. samples were prepared by sealing (under nitrogen) 5-mm. Pyrex tubes containing a mixture of approximately 90% pure liquid compound and 10% benzotrifluoride by volume.

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