

ways determined first by scanning the region 9.5–10.0 without TMS; then TMS was added, the peaks were realigned, and the TMS peak was recorded. A calibration sample was run each day that a spectrum was determined.

**Source of Compounds.**—Except where references to other workers appear, all materials employed were prepared in this laboratory and the syntheses of these materials will appear in a separate publication.

### Halomethyl Metal Compounds. XIII. The Preparation of *gem*-Difluorocyclopropanes by Iodide Ion Induced CF<sub>2</sub> Transfer from Trimethyl(trifluoromethyl)tin<sup>1,2</sup>

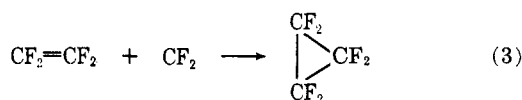
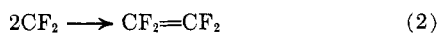
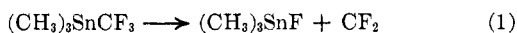
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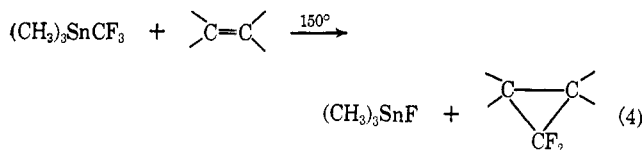
*Received March 8, 1967*

The action of sodium iodide on trimethyl(trifluoromethyl)tin in DME in the presence of an olefin gives *gem*-difluorocyclopropanes in yields ranging from moderate to excellent according to the equation  $\text{Me}_3\text{SnCF}_3 + \text{NaI} + \text{olefin} \rightarrow \text{Me}_3\text{SnI} + \text{NaF} + \text{gem-difluorocyclopropane}$ . It is suggested that the mechanism of this reaction involves nucleophilic attack by iodide ion on tin to displace the trifluoromethyl anion, which then loses fluoride ion to form difluorocarbene. The latter subsequently reacts with the olefin to give the *gem*-difluorocyclopropane. The formation of fluoroform when the  $\text{Me}_3\text{SnCF}_3 + \text{NaI}$  reaction was carried out in acetone-DME provides indirect evidence in favor of such a mechanism. Nineteen new *gem*-difluorocyclopropanes were prepared by this route, including difluorocyclopropyl derivatives of silicon, germanium, and tin. Noteworthy is the observation that CF<sub>2</sub> does not insert into C–H bonds, even into those which are very reactive toward CCl<sub>2</sub>. The pyrolysis of  $\text{Me}_3\text{SnCF}_3$  in the presence of benzoic acid gave difluoromethyl benzoate in 50% yield.

In 1960 Stone and co-workers<sup>6</sup> and Clark and Willis<sup>7</sup> reported the preparation of trimethyl(trifluoromethyl)tin by the reaction of hexamethylditin with iodotrifluoromethane. Of great interest was the finding of the latter group that  $\text{Me}_3\text{SnCF}_3$  decomposed on being heated in a sealed tube at 150° for 20 hr with almost quantitative conversion to trimethyltin fluoride and hexafluorocyclopropane. The formation of the latter was rationalized in terms of initial  $\alpha$  elimination of trimethyltin fluoride, followed by dimerization of the difluorocarbene thus generated and CF<sub>2</sub> addition to the resulting tetrafluoroethylene (eq 1–3). Indeed, pyroly-



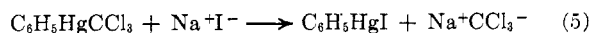
sis of  $\text{Me}_3\text{SnCF}_3$  in the presence of added tetrafluoroethylene gave the expected quantity of hexafluorocyclopropane. The possibility that  $\text{Me}_3\text{SnCF}_3$  might serve in a general preparation of *gem*-difluorocyclopropanes (eq 4) was not investigated by these workers.



Subsequently, the pyrolysis of trifluoromethyl derivatives of iron,<sup>8</sup> phosphorus,<sup>9</sup> and germanium<sup>10</sup> has been observed to generate CF<sub>2</sub>. The pyrolysis of  $\text{CF}_3\text{Fe}(\text{CO})_4\text{I}$  in the presence of ethylene was reported to give 1,1-difluorocyclopropane, but neither yield data nor experimental details were provided.<sup>8</sup> Also of interest is that  $(\text{CF}_3)_3\text{As}$  and  $(\text{CF}_3)_3\text{Sb}$  underwent thermal decomposition at 180–220° to give a mixture of products containing 10% tetrafluoroethylene and hexafluorocyclopropane.<sup>11</sup> Successful transfer of CF<sub>2</sub> to olefins has been achieved *via* decarboxylation of sodium chlorodifluoroacetate in 1,2-dimethoxyethane (DME) or diglyme in the presence of olefins<sup>12,13</sup> or by thermolysis or photolysis of difluorodiazirine in the presence of olefins.<sup>14,15</sup>

Of the CF<sub>2</sub> transfer reagents mentioned above,  $\text{ClCF}_2\text{CO}_2\text{Na}$  was the most useful. The others were somewhat less practical, either because their preparation was difficult or was achieved in only poor yield, or because their pyrolysis required temperatures too high to allow their general application in *gem*-difluorocyclopropane synthesis.

In our work with phenyl(trihalomethyl)mercury compounds we found that phenyl(trichloromethyl)mercury (which releases CCl<sub>2</sub> to olefins at 80°, but which requires rather long reaction times for quantitative decomposition at that temperature) reacts rapidly with sodium iodide in DME at 80° as shown in eq 5.<sup>1,2</sup> The



trichloromethide ion thus produced loses chloride ion, giving dichlorocarbene. If this displacement is carried

(1) Part XII: D. Seyferth, M. E. Gordon, J. Y.-P. Mui, and J. M. Burlitch, *J. Am. Chem. Soc.*, **89**, 959 (1967).

(2) Preliminary communication: D. Seyferth, J. Y.-P. Mui, M. E. Gordon, and J. M. Burlitch, *ibid.*, **87**, 681 (1965).

(3) Alfred P. Sloan Foundation Fellow, 1962–1966.

(4) National Institutes of Health Predoctoral Fellow, 1963–1966.

(5) Postdoctoral Research Fellow, 1963–1965; on leave from the Nitto Chemical Industrial Co., Ltd., Osaka, Japan.

(6) H. D. Kaez, J. R. Phillips, and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6228 (1960).

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(9) W. Mahler, *ibid.*, **84**, 4600 (1962).

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(11) P. B. Ayscough and H. J. Emelús, *J. Chem. Soc.*, 3381 (1954).

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(13) L. H. Knox, E. Velarde, S. Berger, D. Cuadriello, P. W. Landis, and A. D. Cross, *J. Am. Chem. Soc.*, **85**, 1851 (1963).

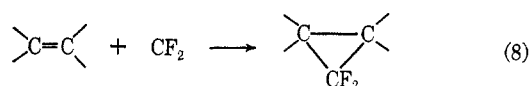
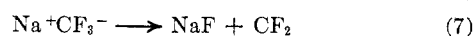
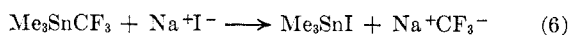
(14) R. A. Mitsch, *ibid.*, **87**, 758 (1965).

(15) R. A. Mitsch, *J. Heterocyclic Chem.*, **1**, 271 (1964).

out in the presence of a suitable olefin, then *gem*-dichlorocyclopropanes can be prepared in excellent yield. These observations suggested that similar displacement of  $\text{CF}_3^-$  by iodide ion from  $\text{Me}_3\text{SnCF}_3$  at temperatures substantially below  $150^\circ$  might be possible. We were encouraged to pursue this idea by a previous report that the action of iodide ion in aqueous solution on  $\text{CF}_3\text{HgI}$  produced fluoroform.<sup>16</sup>

A reaction of 12 mmoles of  $\text{Me}_3\text{SnCF}_3$  and 15 mmoles of sodium iodide in DME in the presence of an excess of cyclohexene at reflux for 12 hr gave trimethyltin iodide (90%) and 7,7-difluoronorcarane (73%) as volatile products. Another such reaction carried out for 20 hr produced 7,7-difluoronorcarane in 89% yield. This reaction is too slow at room temperature to be useful; only a 9% yield of the difluoronorcarane was obtained when these reagents were allowed to react at room temperature for 74 hr. The effect of the sodium iodide was made apparent by heating a solution of trimethyl-(trifluoromethyl)tin and excess cyclohexene in DME for 12 hr without added sodium iodide; 7,7-difluoronorcarane was produced in only 1% yield. In another experiment, the  $\text{Me}_3\text{SnCF}_3 + \text{NaI}$  procedure was used to prepare 1,1-difluorotetramethylcyclopropane from tetramethylethylene in 77% yield. The results demonstrate that the use of the  $\text{Me}_3\text{SnCF}_3 + \text{NaI}$  reagent system represents a valuable new route to *gem*-difluorocyclopropanes. Its advantages lie in the fact that it should be adaptable to fairly large-scale application and that it is carried out at relatively low temperature and at atmospheric pressure. Also, hexamethylditin, from which trimethyl(trifluoromethyl)tin can be prepared in high yield, is now available commercially.<sup>17</sup>

We suggest that the *gem*-difluorocyclopropane synthesis by the  $\text{Me}_3\text{SnCF}_3 + \text{NaI}$  procedure proceeds by the sequence of (eq 6-8). Evidence suggestive of a



trifluoromethyl anion intermediate was obtained by carrying out the  $\text{Me}_3\text{SnCF}_3 + \text{NaI}$  reaction in acetone solution. The protonation product of  $\text{CF}_3^-$ , fluoroform, was isolated in 23% yield. No  $\text{Me}_2(\text{CF}_3)\text{COH}$  was detected.

The reactions of the  $\text{Me}_3\text{SnCF}_3 + \text{NaI}$  reagent with a number of olefins were examined. The results are presented in Table I.

Several of these reactions deserve further discussion. First, with a few exceptions, the yields of *gem*-difluorocyclopropanes obtained by this procedure generally ranged from good to excellent, and they compared favorably with those obtained when difluorodiazirine is used as  $\text{CF}_2$  source.<sup>14</sup> Our reagents gave good results even with some of the less reactive olefins such as vinylsilanes, vinyl acetate, pentafluorostyrene, and 1,1-dichloro-2-vinylcyclopropane. Mitsch<sup>14</sup> has noted that the  $\text{CF}_2$  which did not add to the olefins present in the  $\text{CF}_2\text{N}_2 + \text{olefin}$  reactions was accounted for mostly as tetrafluoroethylene and hexafluorocyclopropane. Although we did not look for these by-

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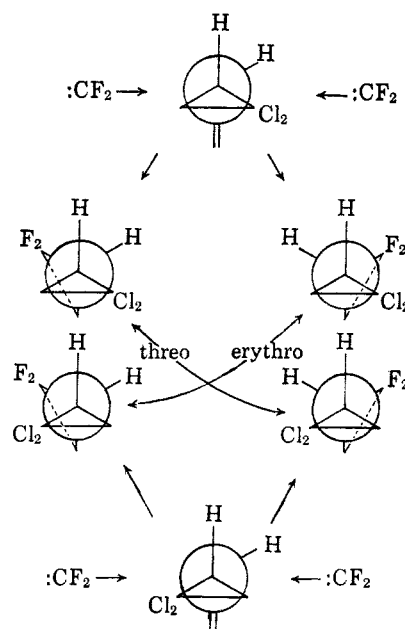
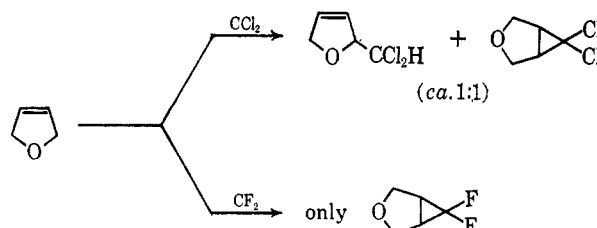


Figure 1.—Formation of *threo* and *erythro* form of 2,2-dichloro-2',2'-difluorobicyclopropyl.

products, it is likely that in the  $\text{Me}_3\text{SnCF}_3 + \text{NaI} + \text{olefin}$  reactions where difluorocyclopropane yields were not high, the  $\text{CF}_2$  balance also is accountable in terms of these products.

The reaction of vinyl acetate with the  $\text{Me}_3\text{SnCF}_3 + \text{NaI}$  reagent is of interest. In its reaction with the  $\text{C}_6\text{H}_5\text{HgCCl}_3 + \text{NaI}$  reagent<sup>1</sup> and with sodium trichloroacetate,<sup>18</sup> this olefin gave both the expected 2,2-dichlorocyclopropyl acetate as well as  $\text{CH}_3\text{CO}_2\text{CH}(\text{CH}_3)\text{CCl}_3$  (which is the product of  $\text{CCl}_3^-$  addition to the  $\text{C}=\text{C}$  bond). In the  $\text{Me}_3\text{SnCF}_3 + \text{NaI} + \text{vinyl acetate}$  reaction *only* the cyclopropane product was obtained. The fact that no  $\text{CH}_3\text{CO}_2\text{CH}(\text{CH}_3)\text{CF}_3$  was formed most likely is due to a very high rate of conversion of  $\text{CF}_3^-$  to  $\text{CF}_2$ , which is the most stable of the dihalocarbenes.<sup>19</sup>

The reaction of the  $\text{Me}_3\text{SnCF}_3 + \text{NaI}$  reagent with 2,5-dihydrofuran also differs markedly from the corresponding reactions of this olefin with various  $\text{CCl}_2$  sources.<sup>20,21</sup> This difference very likely is a manifesta-



tion of the lesser reactivity, hence greater selectivity, of difluorocarbene as compared with dichlorocarbene. The  $\text{Me}_3\text{SnCF}_3 + \text{NaI}$  reaction also was carried out in the presence of isobutyltrimethyltin, a compound




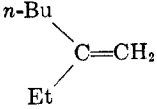







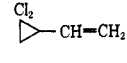

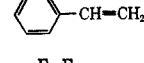

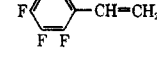










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TABLE I  
 Me<sub>3</sub>SnCF<sub>3</sub> + NaI + OLEFIN REACTIONS

Olefin	Product	% yield	Registry no.	n <sub>D</sub> <sup>20</sup>	Analysis: found (calcd)		
					C, %	H, %	F, %
		89		1.4129 <sup>e</sup>			
Me <sub>2</sub> C=CMe <sub>2</sub>		77	823-25-6	1.3772	62.14 (62.64)	8.92 (9.01)	
		92	13343-31-2	1.3924	66.52 (66.63)	9.91 (9.94)	23.61 (23.43)
Me <sub>2</sub> C=CEt <sub>2</sub>		68	13343-32-3	1.4004	66.73 (66.63)	9.55 (9.94)	23.85 (23.43)
MeCH=CEt <sub>2</sub>		37	13343-33-4		64.80 (64.84)	9.50 (9.52)	25.72 (25.64)
n-C <sub>5</sub> H <sub>11</sub> CH=CH <sub>2</sub>		71	13343-34-5	1.3813	65.00 (64.84)	9.31 (9.52)	25.71 (25.64)
<i>cis</i> -n-PrCH=CHEt		55 <sup>a</sup>	13343-35-6	1.3827	64.94 (64.84)	9.46 (9.52)	25.50 (25.64)
<i>trans</i> -n-PrCH=CHEt		74 <sup>b</sup>	13343-36-7	1.3786	64.74 (64.84)	9.41 (9.52)	25.74 (25.64)
EtMe <sub>2</sub> CCH=CH <sub>2</sub>		36	13343-37-8	1.3849	64.66 (64.84)	9.60 (9.52)	25.79 (25.64)
		Isomer A, 36 <sup>c</sup> Isomer B, 42 <sup>d</sup>	13343-38-9 13343-39-0	1.4369 1.4412	39.00 (38.53) 38.36 (38.53)	3.12 (3.23) 3.19 (3.23)	20.19 (20.42) <sup>f</sup> 20.42 (20.42)
		67	13343-40-3	1.4820	69.98 (70.12)	5.35 (5.23)	24.46 (24.66)
		61	13319-98-7	1.4122	43.84 (44.28)	1.27 (1.24)	54.61 (54.48)
CH <sub>3</sub> CO <sub>2</sub> CH=CH <sub>2</sub>		53	13343-41-4	1.3748	44.03 (44.12)	4.20 (4.44)	28.10 (27.92)
EtMe <sub>2</sub> SiCH=CH <sub>2</sub>		45	13343-42-5	1.3962	50.73 (51.18)	8.77 (8.59)	23.67 (23.08)
Et <sub>3</sub> SiCH=CH <sub>2</sub>		22	13318-44-0	1.4190	56.26 (56.21)	9.55 (9.43)	19.87 (19.76)
Et <sub>3</sub> GeCH=CH <sub>2</sub>		39	13343-43-6	1.4253	46.63 (46.64)	8.03 (7.66)	16.42 (16.06)
Et <sub>3</sub> SnCH=CH <sub>2</sub>		52	13343-44-7	1.4576	38.42 (38.20)	6.36 (6.41)	13.54 (13.43)
Me <sub>3</sub> SiCH <sub>2</sub> CH=CH <sub>2</sub>		80	13396-32-2	1.3899	51.62 (51.18)	8.75 (8.59)	
Me <sub>3</sub> SnCH <sub>2</sub> CH=CH <sub>2</sub>		54	13343-45-8	1.4450	33.00 (32.98)	5.60 (5.54)	15.29 (14.91)
		56 in DME 66 in diglyme	13343-46-9	1.3942	50.14 (50.00)	4.76 (5.04)	31.71 (31.64)
CCl <sub>2</sub> =CHCl	No reaction (95% recovery)						
CCl <sub>2</sub> =CCl <sub>2</sub>	No reaction						

<sup>a</sup> Retention time 10 min, 7 sec (20% SE-30 on Chromosorb W, 65° isothermal, 50 cc of helium/min flow rate). <sup>b</sup> Retention time 8 min, 15 sec under the conditions given in footnote a. <sup>c</sup> Retention time 7 min, 48 sec (20% SE-30 on Chromosorb W, 90° isothermal, 50 cc of helium/min flow rate). <sup>d</sup> Retention time 9 min under conditions given in footnote c. <sup>e</sup> Lit.<sup>12</sup> n<sub>D</sub><sup>20</sup> 1.4130. <sup>f</sup> Anal. Calcd: Cl, 37.92. Found (for isomer A): Cl, 37.87. Found (for isomer B): Cl, 37.91.

which reacts with C<sub>6</sub>H<sub>5</sub>HgCCl<sub>2</sub>Br at 80° to give Me<sub>3</sub>SnCH<sub>2</sub>CMe<sub>2</sub>CCl<sub>2</sub>H in high yield.<sup>22</sup> In this case also no product of CF<sub>2</sub> insertion into a C-H bond was observed. Apparently, other CF<sub>2</sub> reactions (olefin addition, and/or C<sub>2</sub>F<sub>4</sub> formation) are more favorable

than insertion into C-H bonds, even into those which are especially reactive toward dichlorocarbene.

Mitsch<sup>14</sup> has shown that CF<sub>2</sub> (via CF<sub>2</sub>N<sub>2</sub> photolysis) adds to *cis*- and *trans*-2-butene in a stereospecific manner. The fact that different products were obtained in the reaction of the Me<sub>3</sub>SnCF<sub>3</sub> + NaI reagent with *cis*- and *trans*-3-heptene, respectively, is in agreement with this finding.

(22) D. Seyferth and S. S. Washburne, unpublished work. See the preliminary communication on this general type of reaction: D. Seyferth and S. S. Washburne, *J. Organometal. Chem.* (Amsterdam), **5**, 389 (1966).

It will be noted that the reaction of the  $\text{Me}_3\text{SnCF}_3 + \text{NaI}$  reagent with 1,1-dichloro-2-vinylcyclopropane gave two products which were shown to be isomers. A total of four isomeric  $\text{CF}_2$  addition products is expected in this case in view of the fact that the adduct contains two asymmetric carbon atoms, the *threo* and *erythro* forms, each as a pair of enantiomers (see Figure 1). A separation of the *threo* and *erythro* forms, which will differ in physical properties, thus has been effected by glpc. The fact that they were formed in nearly equal amounts suggests that approach of  $\text{CF}_2$  must be facile from either side of the double bond. No attempt was made to equate the structures of isomers A and B with the *threo* and *erythro* forms.

Another reaction which both  $\text{CCl}_2$  (via  $\text{C}_6\text{H}_5\text{HgCCl}_2\text{-Br}$ )<sup>23</sup> and  $\text{CF}_2$  (via  $\text{CF}_2\text{N}_2$ )<sup>24</sup> undergo is insertion into the O-H bond of carboxylic acids. As might be expected in terms of the process shown in eq 6 and 7, the  $\text{Me}_3\text{SnCF}_3 + \text{NaI}$  system is not suitable for conversion of carboxylic acids to their difluoromethyl esters. No products of this type were formed with acetic or benzoic acids. However, pyrolysis of trimethyl(trifluoromethyl)tin in a sealed tube at 155° in the presence of benzoic acid gave  $\text{C}_6\text{H}_5\text{CO}_2\text{CF}_2\text{H}$  in 50% yield.

This study and other work reported from these laboratories<sup>25</sup> have shown that trihalomethyltin compounds are useful  $\text{CX}_2$  transfer agents, and our efforts in this area of organotin chemistry are continuing.

### Experimental Section

**General Comments.**—Elemental analyses were performed by Dr. S. M. Nagy (Massachusetts Institute of Technology Microchemical Laboratory) and the Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded for pure liquid films on a Perkin-Elmer Infracord 337. Proton magnetic resonance spectra were obtained (in  $\text{CCl}_4$  solution) using a Varian Associates A-60 nmr spectrometer. Gas-liquid partition chromatography (glpc) was carried out using either an MIT isothermal unit (20% General Electric Co. SE-30 silicone rubber gum on Chromosorb W, 15–20 psi of helium) or an F & M Model 700 gas chromatograph (20% SE-30 on Chromosorb W, temperature programmed). The internal standard procedure was used in yield determinations.









All reactions were carried out under an atmosphere of purified nitrogen. The DME was distilled from potassium immediately before use.

**Starting Materials.**—The olefins used either were purchased or prepared by standard literature methods. Their purity was assessed by glpc and by comparing their refractive indices and/or infrared spectra with those reported by previous workers. Hexamethylditin was prepared by the procedure of Kraus and Sessions<sup>26</sup> in the early stages of this work and later was obtained from M & T Chemicals, Inc., Rahway, N. J. Trimethyl(trifluoromethyl)tin was prepared in generally excellent yield by irradiation of a mixture of hexamethylditin and trifluoromethyl iodide (purchased from Peninsular ChemResearch, Inc.).<sup>6</sup> Reagent grade sodium iodide was powdered and heated at 110° (0.01 mm) for 24 hr before use.

**The  $\text{Me}_3\text{SnCF}_3 + \text{NaI} + \text{Olefin}$  Reaction.**—Typically, a mixture of the olefin (25 mmoles), trimethyl(trifluoromethyl)tin (20 mmoles), and sodium iodide (20 mmoles) in 12 ml of DME in a 50 ml, three-necked flask equipped with a condenser, nitrogen inlet tube, and magnetic stirring assembly was heated (with stirring) at reflux for 16 hr. The reaction mixture was cooled

TABLE II

INFRARED SPECTRA OF  
SOME *gem*-DIFLUOROCYCLOPROPANES

Compound	Infrared spectrum, $\text{cm}^{-1}$
	3010 (m), 2970 (s), 2940 (s), 2880 (m), 2740 (w), 1485 (s), 1430 (s), 1380 (w), 1370 (m), 1260 (w), 1222 (s), 1152 (s), 1135 (s), 1100 (sh), 998 (s), 967 (m), 895 (w), 825 (m), 684 (m), 595 (w), in $\text{CCl}_4$
$n\text{-C}_5\text{H}_{11}\text{CF}_2$	3085 (w), 3020 (m), 2970 (s), 2935 (s), 2870 (s), 1475 (s), 1390 (s), 1295 (s), 1235 (s), 1205 (s), 1118 (m), 1025 (s), 908 (s), 845 (w), 730 (s), 698 (m)
	3030 (m), 2980 (s), 2950 (s), 2895 (s), 1480 (s), 1370 (m), 1290 (m), 1270 (m), 1235 (m), 1200 (s), 1130 (s), 980 (m), 950 (m), 930 (s), 770 (m)
	3020 (m), 2980 (s), 2950 (s), 2890 (s), 1480 (s), 1475 (s), 1460 (s), 1455 (s), 1380 (m), 1280 (m), 1265 (s), 1240 (s), 1200 (s), 1155 (m), 1075 (m), 1060 (s), 1000 (m), 975 (m), 925 (m), 780 (m)
	3140 (m), 3080 (m), 3060 (m), 1475 (s), 1455 (sh), 1420 (s), 1355 (s), 1280 (s), 1220 (s), 1180 (m), 1125 (s), 1100 (s), 1040 (s), 1020 (s), 915 (s), 900 (s), 800 (m), 770 (s)
	3100 (m), 3040 (sh), 3010 (m), 1480 (s), 1440 (m), 1390 (m), 1355 (s), 1315 (s), 1290 (s), 1240 (sh), 1225 (s), 1195 (s), 1120 (s), 1108 (sh), 1078 (s), 1060 (s), 1040 (s), 1020 (s), 975 (s), 960 (s), 910 (s), 875 (m), 780 (s), 760 (s), 712 (s)
	3090 (m), 3060 (m), 3040 (s), 1950 (w), 1880 (w), 1810 (w), 1755 (w), 1620 (s), 1520 (s), 1475 (s), 1450 (s), 1390 (s), 1350 (s), 1325 (s), 1310 (s), 1230 (s), 1195 (s), 1150 (s), 1095 (s), 1050 (m), 1020 (s), 960 (s), 935 (s), 915 (m), 898 (m), 780 (m), 742 (s), 699 (s), 618 (s)
	3130 (w), 3040 (w), 2940 (w), 2670 (w), 2440 (w), 1750 (w), 1660 (s), 1540 (s), 1500 (s), 1480 (s), 1450 (s), 1390 (s), 1340 (s), 1300 (s), 1235 (s), 1160 (m), 1145 (m), 1095 (m), 1065 (s), 1040 (s), 1005 (s), 950 (s), 910 (s), 860 (s), 790 (s), 750 (w), 740 (w), 715 (m), 670 (w), 605 (w)
$\text{CH}_3\text{CO}_2\text{CF}_2$	3100 (m), 3050 (m), 2920 (m), 1760 (s), 1480 (s), 1370 (s), 1310 (s), 1240 (s), 1210 (s), 1130 (s), 1020 (s), 1010 (s), 980 (m), 910 (s), 740 (m)
$\text{Et}_3\text{SiCF}_2$	3020 (w), 2960 (s), 2920 (s), 2880 (s), 2805 (w), 1460 (s), 1425 (m), 1360 (s), 1275 (s), 1248 (m), 1180 (s), 1090 (s), 1050 (s), 1025 (s), 1010 (sh), 950 (m), 915 (s), 885 (m), 740 (s), 720 (s), 698 (w), 675 (w)
$\text{Et}_3\text{GeCF}_2$	3008 (w), 3002 (m), 2960 (s), 2935 (sh), 2920 (s), 2875 (s), 2840 (s), 2735 (w), 1500 (s), 1480 (m), 1415 (s), 1260 (s), 1172 (s), 1084 (s), 1045 (s), 1020 (s), 940 (s), 908 (s), 880 (m), 710 (s), 605 (s), 580 (s)
$\text{Et}_3\text{SnCF}_2$	3070 (w), 3000 (m), 2960 (s), 2910 (s), 2870 (s), 2820 (m), 2730 (w), 2145 (w), 1460 (s), 1425 (m), 1360 (s), 1248 (s), 1195 (m), 1160 (s), 1080 (s), 1035 (s), 1018 (s), 950 (m), 928 (s), 905 (s), 870 (s), 670 (s)
	3070 (w), 2970 (m), 2945 (m), 2875 (s), 1480 (m), 1460 (s), 1450 (s), 1365 (s), 1275 (m), 1260 (s), 1160 (s), 1080 (s), 1060 (s), 1000 (m), 960 (s), 890 (m), 825 (m), 730 (m)

(23) D. Seyferth and J. Y.-P. Mui, *J. Am. Chem. Soc.*, **88**, 4672 (1966).

(24) R. A. Mitsch and J. E. Robertson, *J. Heterocyclic Chem.*, **2**, 152 (1965).

(25) D. Seyferth, F. M. Armbrecht, Jr., B. Prokai, and R. J. Cross, *J. Organometal. Chem.* (Amsterdam), **6**, 573 (1966).





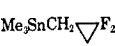

(26) C. A. Kraus and W. V. Sessions, *J. Am. Chem. Soc.*, **47**, 2361 (1925).

and anhydrous ammonia was bubbled in slowly in order to remove the trimethyltin iodide formed as the insoluble ammoniate.<sup>27</sup> The latter was removed by filtration. The filtrate was distilled at 0.05–0.1 mm (pot temperature as low as practically possible) into a receiver cooled to  $-78^{\circ}$ . In most cases the product yields were determined by glpc analysis of the distillate and product samples for elemental analysis, spectroscopic studies, etc., were isolated by preparative glpc.

Yields, refractive indices, and analytical data are given in Table I. Table II lists the infrared spectra of a number of the new compounds obtained. C–F absorptions generally are found in the region  $1400\text{--}1000\text{ cm}^{-1}$ ,<sup>28</sup> and Mitsch<sup>14</sup> has noted that absorption in the  $1470\text{--}1495\text{ cm}^{-1}$  region is characteristic of *gem*-difluorocyclopropanes. The proton magnetic resonance spectra of a few of the products are given in Table III.

TABLE III

 PROTON MAGNETIC RESONANCE SPECTRA  
 OF SOME *gem*-DIFLUOROCYCLOPROPANES

Compound	Nmr spectrum <sup>a</sup>
	Triplet at 1.08 ( $J_{\text{HF}} = 2.0$ cps)
	Multiplet between 0.7 and 1.25 ( $\text{CH}_3$ and cyclopropane H's); complex absorption, 1.25–1.6 ( $\text{CH}_2$ of Et and <i>n</i> -Bu)
	Triplet at 0.92 ( $J_{\text{HH}} = 7.5$ cps; $\text{CH}_3\text{CH}_2$ ); triplet at 1.14 ( $J_{\text{HF}} = 2.0$ cps; $\text{CH}_3$ ); quartet at 1.48 ( $J_{\text{HH}} = 7.5$ cps; $\text{CH}_3\text{--CH}_2$ ), with fine splitting into triplet, $J_{\text{HF}} = 2.0$ cps.
	Multiplet at 1.16–1.95 ( $\text{CH}_2$ of cyclopropane ring); singlet at 1.98 ( $\text{CH}_3$ ); multiplet at 3.85–4.43 ( $\text{HCOCOCH}_3$ )
	Singlet at 0.11 ( $J_{\text{Sn}^{117}\text{--H}^1} = 50$ cps; $J_{\text{Sn}^{119}\text{--H}^1} = 54$ cps); complex multiplet between 0.58 and 1.65
	Doublet at 2.28 ( $J_{\text{HF}} = 12$ cps, with fine splitting; cyclopropane hydrogens); complex multiplet at 3.23–4.25 ( $\text{CH}_2$ )

<sup>a</sup> Chemical shifts in parts per million downfield from internal tetramethylsilane.

(27) (a) A. Cahours, *Ann.*, **122**, 56 (1862); (b) A. Werner, *Z. Anorg. Allgem. Chem.*, **17**, 97 (1898).

(28) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Methuen and Co., London, 1958, p 329.

**The  $\text{Me}_3\text{SnCF}_3 + \text{NaI}$  Reaction in Acetone–DME.**—Into a 50-ml, three-necked flask equipped with a condenser, a magnetic stirring assembly, a nitrogen inlet tube, and an exit tube leading to a trap immersed in liquid nitrogen was charged 10 mmoles of trimethyl(trifluoromethyl)tin, 20 mmoles of sodium iodide, 20 ml of anhydrous acetone, and 10 ml of DME. The reaction mixture was heated at reflux (with stirring) for 16 hr. The contents of the  $-196^{\circ}$  trap (acetone and fluoroform) then were fractionated on a high vacuum system. Appropriate vapor pressure measurements showed that 2.3 mmoles of fluoroform was present. This product was identified by comparing its mass spectrum with that of an authentic sample (Peninsular ChemResearch).

The reaction solution was distilled at 0.05 mm into a receiver at  $-78^{\circ}$ . Glpc analysis of the distillate showed that the volatiles present were acetone, DME, and trimethyltin iodide. No  $\text{Me}_2(\text{CF}_3)\text{COH}$  was present; an authentic sample of the latter had been prepared by the reaction of trifluoroacetic anhydride with excess  $\text{MeMgBr}$ .<sup>29</sup> The tetrafluoroethylene that might also have been expected in this experiment may have polymerized under the reaction conditions.

**Pyrolysis of Trimethyl(trifluoromethyl)tin in the Presence of Benzoic Acid.**—A nitrogen-flushed, heavy-walled Pyrex bomb tube was filled with 9 mmoles of benzoic acid, 10 mmoles of  $\text{Me}_3\text{SnCF}_3$ , and 10 ml of dry benzene, cooled to  $-78^{\circ}$ , evacuated to 1 mm and sealed. It then was heated at  $155^{\circ}$  for 20 hr. Appreciable gas pressure (tetrafluoroethylene and fluoroform?) was noticeable when the tube was opened at  $-78^{\circ}$ . The reaction mixture was filtered. The white solid thus removed was washed with dilute sodium bicarbonate solution, water, and a small amount of ethanol to give 1.18 g (65%) of trimethyltin fluoride. Glpc analysis (20% SE-30 on Chromosorb W,  $100^{\circ}$  column temperature, 45 cc of helium/min flow rate) showed the presence of two volatile products. The major product was difluoromethyl benzoate<sup>24</sup> (50%). Its infrared spectrum (pure liquid film) showed bands at 3080 (w), 3050 (w), 1775 (s), 1610 (m), 1470 (m), 1380 (w), 1325 (w), 1270 (s), 1260 (sh), 1180 (m), 1150 (s), 1112 (sh), 1075 (s), 1030 (s), 1010 (m), 870 (w), 810 (w), 720 (s), and 680 (m)  $\text{cm}^{-1}$ . Its proton nmr spectrum (in  $\text{CCl}_4$ ) showed a triplet centered at 7.27 (1 H,  $J_{\text{HF}} = 71$  cps) and two multiplets centered at 7.55 and 8.08 ppm (5 H).

**Registry No.**—Difluoromethyl benzoate, 1885-09-2; trimethyl(trifluoromethyl)tin, 754-25-6.

**Acknowledgments.**—The authors are grateful to the Directorate of Chemical Sciences, Air Force Office of Scientific Research, for generous support of this work and to M & T Chemicals, Inc., for gifts of chemicals. This work was supported in part by Public Health Service Fellowship 5-F1-GM-20,179 (to H. D.).

(29) R. H. Groth, *J. Org. Chem.*, **24**, 1709 (1959).