# Halomethyl Metal Compounds. LX. Phenyl(trifluoromethyl)mercury: a Useful Difluorocarbene Transfer Agent<sup>1</sup>

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The reaction of phenyl(trifluoromethyl)mercury and 3 molar equiv of anhydrous sodium iodide in benzene medium in the presence of olefins serves excellently in the synthesis of gem-diffuorocyclopropanes. High product yields are obtained in reaction times of about 15 hr at 80-85°. Since PhHgCFs is now relatively easily prepared, this represents a very useful new CF<sub>2</sub> transfer system. Phenyl(trifluoromethyl)mercury, which does not release CF2 at 140°, reacts with triorganotin halides to give R<sub>3</sub>SnCF3 compounds and phenylmercuric halide. When this reaction is carried out at 130° in the presence of cyclooctene, 9,9-diffuorobicyclo [6.1.0] nonane is formed in moderate yield.

There are many compounds whose thermolysis or photolysis produces diffuorocarbene.<sup>2</sup> The reagent most utilized in synthetic applications is CClF<sub>2</sub>CO<sub>2</sub>--Na+, which undergoes decarboxylation and loss of chloride ion in diglyme solution at 125-140°. Other  $CF_2$  precursors are less practical, either because they are difficult to prepare, not readily available, hazardous to handle, or too stable for application at the usual temperatures  $(25-150^\circ)$  of organic synthesis. Among the  $CF_2$  generators studied have been some trifluoromethyl metal compounds, including trimethyl(trifluoromethyl)tin,<sup>3</sup> trifluoromethylgermanium triiodide,<sup>4</sup> trifluoromethyliron tetracarbonyl iodide,<sup>5</sup> and tris-(trifluoromethyl)difluorophosphorane.<sup>6</sup> More recently, trifluoromethyltrifluorosilane has been added to this list.<sup>7</sup> Clark and Willis,<sup>8</sup> the original discoverers of the CF<sub>2</sub> transfer capability of trimethyl(trifluoromethyl)tin, only carried out its thermolysis at 150° in the presence of tetrafluoroethylene (a reaction which gave a quantitative yield of hexafluorocyclopropane), but Cullen and his coworkers have used this reagent to add  $CF_2$  to various fluorinated olefins and acetylenes containing group IV and group V organometallic substituents<sup>8</sup> and to insert CF<sub>2</sub> into the Sn-H bond of trimethyltin hydride.<sup>9</sup> In an earlier investigation, we showed that the action of sodium iodide in 1,2-dimethoxyethane (DME) at  $80-85^{\circ}$  leads to release of  $CF_2$  as shown in eq 1. When this reaction was carried

$$Me_{3}SnCF_{3} + Na^{+}I^{-} \longrightarrow Me_{3}SnI + Na^{+}CF_{3}^{-} \downarrow \downarrow NaF + CF_{2} \quad (1)$$

out in the presence of olefins, gem-diffuorocyclopropanes were produced in yields ranging from moderate to

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excellent, depending on the nature of the olefin.<sup>10</sup> This is one of the mildest procedures for the generation of diffuorocarbene in solution, but a drawback to the more general application of our reagent system in synthesis was the fact that trimethyl(trifluoromethyl)tin is neither commercially available nor readily prepared from commercially available materials. Its synthesis is based on trimethyltin chloride and the expensive iodotrifluoromethane (eq 2, 3).<sup>3,11</sup> Furthermore, once

$$2Me_{\mathfrak{s}}SnCl \xrightarrow{Na} Me_{\mathfrak{s}}Sn-SnMe_{\mathfrak{s}}$$
(2)

 $Me_8Sn-SnMe_4 + CF_3I \xrightarrow{\text{sealed tube, uv}} Me_8SnCF_4 + Me_8SnI$  (3)

prepared, Me<sub>3</sub>SnCF<sub>3</sub> must be handled with suitable precautions, since it is unstable to atmospheric moisture. The  $CF_3$  metal derivatives are even less practical. These considerations led us to devote some attention to the possible application of trifluoromethyl mercury compounds as  $CF_2$  precursors. In view of the successful development of phenyl(trihalomethyl)mercury compounds such as PhHgCCl<sub>3</sub>, PhHgCCl<sub>2</sub>Br, PhHgCClBr<sub>2</sub>, PhHgCBr<sub>3</sub>,<sup>12</sup> PhHgCCl<sub>2</sub>F,<sup>1,13</sup> PhHgCCl<sub>2</sub>I,<sup>14</sup> PhHgCCl-BrI,<sup>15</sup> and PhHgCBr<sub>2</sub>F<sup>15</sup> as dihalocarbene transfer agents, the organomercurial of choice for the purposes of the present study was phenyl(trifluoromethyl)mercury, a compound still unknown at the outset of this investigation. Strong support for this intended investigation also was provided by the fact that, for the trichloromethyl and bromodichloromethyl systems, the respective PhHgCX<sub>3</sub> compound was quite more reactive in CX<sub>2</sub> transfer chemistry than was the analogous Me<sub>3</sub>SnCX<sub>3</sub> compound.<sup>16</sup>

In previous papers of this series we have described routes to phenyl(trifluoromethyl)mercury.<sup>17,18</sup> Its prep-

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aration can be effected most simply and cheaply by the sequence shown in eq 4-7. In the present report we

$$HgO + 2CF_{3}CO_{2}H \longrightarrow Hg(O_{2}CCF_{3})_{2} + H_{2}O \qquad (4)$$

$$Hg(O_2CCF_3)_2 \xrightarrow{OOO} CF_3HgO_2CCF_3 + CO_2$$
(5)

$$CF_{3}HgO_{2}CCF_{3} + Ph_{2}Hg \longrightarrow PhHgCF_{3} + PhHgO_{2}CCF_{3}$$
 (6)

 $PhHgO_2CCF_3 + NH_4+Cl^{-} \xrightarrow{H_2O} PhHgCl_1 + NH_4+O_2CCF_3^{-}$ (7)

3000

describe the application of  $PhHgCF_3$  as a very useful  $CF_2$  reagent.

#### **Results and Discussion**

All of the phenyl(trihalomethyl)mercury compounds mentioned above undergo thermal dihalocarbene extrusion in the temperature range 25-80°. Rate measurements and the fact that PhHgCCl<sub>2</sub>F eliminated phenylmercuric chloride exclusively established the sequence PhHgI > PhHgBr > PhHgCl > PhHgF for the ease of  $\alpha$  elimination of phenylmercuric halide from phenyl-(trihalomethyl)mercurials. It might therefore have been expected that the rate of  $CF_2$  extrusion from Ph- $HgCF_3$  at 80° would be very slow. In actual fact, this reaction did not appear to take place at all. Phenyl-(trifluoromethyl)mercury remained undecomposed after it had been heated in cyclooctene at reflux (140°) for 10 days.

This unexpected lack of reactivity of PhHgCF<sub>3</sub> on being heated in the presence of an olefin, however, did not preclude its use as a  $CF_2$  transfer agent. The sodium iodide procedure, which had been applied to good advantage to the generation of  $CF_2$  from trimethyl(trifluoromethyl)tin (eq 1), had been developed first to facilitate CCl<sub>2</sub> release from PhHgCCl<sub>3</sub>.<sup>10a,19</sup> Thus we expected that sodium iodide would react with phenyl(trifluoromethyl)mercury to give CF<sub>2</sub> via intermediate  $CF_3$ <sup>-</sup>. Further experiments showed this to be the case.

In previous applications of the sodium iodide procedure to dihalocarbene generation,<sup>10,19</sup> we found that the reactions proceeded best when DME, in which sodium iodide is soluble, was used as reaction medium. In contrast, the PhHgCF<sub>3</sub>/NaI/olefin reactions did not require DME as solvent and, in fact, they proceeded readily in dry benzene medium in which sodium iodide is not soluble to an appreciable extent. In the CF<sub>2</sub> transfer reactions as developed, 1 molar equiv of PhHgCF<sub>3</sub> was allowed to react with 3 molar equiv of anhydrous sodium iodide in the presence of 3 molar equiv of the olefin in benzene solution at reflux. The progress of the reactions was followed by thin layer chromatographic (tlc) monitoring of the consumption of PhHgCF<sub>3</sub>; reaction times of 15-20 hr (at 80°) appeared to be required. Alternatively, the reaction could be carried out in the absence of an inert diluent. using the olefin itself as reaction medium. The  $CF_2$ transfer reactions thus were quite simple to carry out, and subsequent work-up of the reaction mixtures proceeded without difficulty. Filtration removed phenylmercuric iodide and the sodium salts (NaI and NaF) and the product gem-difluorocyclopropane in the fil-

trate could be isolated by distillation or by gas chromatography. That DME is not required as reaction medium and that benzene may be used in its place was surprising. The enhanced Lewis acidity of the mercury atom in PhHgCF<sub>3</sub> (compared to PhHgCCl<sub>3</sub>) owing to the highly electronegative<sup>20</sup> CF<sub>3</sub> substituent probably is an important factor which results in this observation. In any case, the ability to use the easily purified benzene in place of DME, which is relatively difficult to maintain pure, represents a substantial improvement in procedure.

The reactions carried out with the PhHgCF<sub>3</sub>/NaI reagent are summarized in Table I. The yields of the desired gem-difluorocyclopropane in general were quite good. It is not surprising that the more electrophilic olefins (acrylonitrile, the vinylsilanes) gave lower product yields. We note that the reactions with cis- and trans-3-hexene were stereospecific, in agreement with previous findings of Mitsch<sup>21</sup> on diffuorocyclopropanation of cis- and trans-2-butene using difluorodiazirine as  $CF_2$  source. The absence of a  $CF_3$ adduct in the case of vinyl acetate and of CH insertion of  $CF_2$  in the case of 2,5-dihydrofuran found in these reactions of PhHgCF<sub>3</sub>/NaI are observations already made and commented on previously in our study of the Me<sub>3</sub>SnCF<sub>3</sub>/NaI system.<sup>10b</sup> No CF<sub>3</sub>- adduct was formed in the reaction of PhHgCF<sub>3</sub>/NaI with acrylonitrile, in contrast to the formation of CCl<sub>3</sub>CH<sub>2</sub>-CH<sub>2</sub>CN in the reaction of PhHgCCl<sub>3</sub>/NaI with this olefin.19

Some compounds which normally are reasonably good carbenophiles in the case of CCl<sub>2</sub> or CClF did not react with the PhHgCF<sub>3</sub>/NaI reagent. Among these were cumene, thiobenzophenone, sym-dichlorotetrafluoroacetone, diethyl azodicarboxylate, and PhN=  $CCl_2$ . For example, the  $PhHgCCl_2F/NaI$  reagent was found to convert PhN=CCl<sub>2</sub> to 1-phenyl-2-fluoro-2,3,3-trichloroaziridine in 70% yield,<sup>1</sup> but PhN=CCl<sub>2</sub> was recovered unchanged after the PhHgCF<sub>3</sub>/NaI reaction had been carried out in its presence.

An alternate but rather less useful procedure for releasing CF<sub>2</sub> from phenyl(trifluoromethyl)mercury is based on the well-known ability of organomercurials to undergo alkyl(or aryl)-for-halogen exchange with halides of other metals.<sup>22</sup> Thus PhHgCF<sub>3</sub>, which, as mentioned already, does not react with cyclooctene at 140° during a 10-day reaction time, was found to transfer CF<sub>2</sub> to this olefin under these conditions, giving 9,9-difluorobicyclo [6.1.0] nonane in 56% yield when 3 molar equiv of tri-n-butyltin bromide was present in the reaction mixture. Tri-n-butyltin chloride was equally effective, triphenyltin bromide less so. Although a halogen exchange between PhHgCF<sub>8</sub> and n-Bu<sub>3</sub>SnBr, to give PhHgCF<sub>2</sub>Br and n-Bu<sub>3</sub>SnF, might be considered a possible rationalization of these results, experiments with trimethyltin bromide suggested that the actual reaction course is that shown in eq 8 and 9. Such exchange (eq 8) was demonstrated in a reaction in which PhHgCF<sub>3</sub> and 3 molar equiv of trimethyltin bromide were heated in chlorobenzene for 4 days at 130°. At the end of this time, both

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REACTIONS OF THE PhHgCF <sub>8</sub> /NaI REAGENT WITH OLEFINS				
Olefin	Registry no.	Product	(% yield)	Registry no.
$\bigcirc$	110-83-8	$\sum F_2$	(83)	
$\bigcirc$	931-88-4	$\frown$ $F_2$	(83)	36601-95-3
$C_{2}H_{5}$ $C_{3}H_{5}$ $C=C$ $H$ $H$	7642-09-3	C <sub>2</sub> H <sub>5</sub> H F F	(93)	36601-9 <b>6-4</b>
$C_{2}H_{5}$ H C==C H $C_{2}H_{5}$	13269-52-8	$C_{2}H_{3}$ $H$ $C_{2}H_{5}$ $H$ $C_{2}H_{5}$	(94)	36597-13-4
n-C <sub>5</sub> H <sub>11</sub> CH=CH <sub>2</sub>	592-76-7	n-C <sub>5</sub> H <sub>11</sub>	(70)	
Me <sub>3</sub> SiCH <sub>2</sub> CH=CH <sub>2</sub>	762-72-1	Me <sub>3</sub> SiCH <sub>2</sub> F	(100)	
$Me_2EtSiCH=-CH_2$	18163-06-9	Me,EtSi F	(44)	
Me <sub>8</sub> SiCH=CH <sub>2</sub>	754-05-2	Me <sub>s</sub> Si F	(53)	19097-34-8
$\langle _{0} \rangle$	1708-29-8	F O	(67)	
CH <sub>3</sub> CO <sub>2</sub> CH=CH <sub>2</sub>	108-05-4	CH <sub>2</sub> CO <sub>2</sub> F	(84)	
CH₂=CHCN	75-05-8	NC F F F	(26)	36597-03-2
CCl₂=−CHCl	79-01-6		(72)	36597-04-3

TABLE I

 $PhHgCF_3 + n \cdot Bu_3SnX \implies PhHgX + n \cdot Bu_3SnCF_3$  (8)  $\rightarrow$  n-Bu<sub>3</sub>SnF +  $n \cdot Bu_3 Sn CF_3 +$ (9)

PhHgBr and the known Me<sub>3</sub>SnCF<sub>3</sub> could be isolated and identified. Such exchange reactions generally are equilibrium processes, and this is true also in the present case. A reaction of equimolar amounts of  $Me_8SnCF_3$  and phenylmercuric bromide in chloro-benzene at 130° for 3 days gave some PhHgCF<sub>3</sub> and trimethyltin bromide.

Finally, a discussion of other CF<sub>3</sub>Hg compounds as CF<sub>2</sub> sources is appropriate, although PhHgCF<sub>3</sub> remains

the reagent of choice. In our synthesis of PhHgCF<sub>3</sub>, the compound CF<sub>3</sub>HgO<sub>2</sub>CCF<sub>3</sub> was an intermediate (eq 5 and 6), and CF<sub>3</sub>HgCl, CF<sub>3</sub>HgBr, and CF<sub>3</sub>HgI also were prepared during the course of this study. An assessment of their possible utility as CF<sub>2</sub> transfer agents was of interest. Of these four CF<sub>3</sub>HgX compounds, only CF3HgI served satisfactorily. Its reaction with 3 molar equiv of sodium iodide in the presence of cyclohexene in benzene at reflux proceeded with precipitation of red mercuric iodide and gave 7,7diffuoronorcarane in 88% yield. A similar reaction carried out in the presence of allyltrimethylsilane gave 1, 1- diffuoro-2- (trimethyl silyl methyl) cyclopropanein 78% yield. However, trifluoromethylmercuric iodide is light sensitive and not very stable to storage at room temperature. Also, it is rather volatile and thus  $PhHgCF_3$  is, in our opinion, a clearly superior  $CF_2$  reagent.

No gem-diffuorocyclopropane was formed when  $CF_{3}HgO_{2}CCF_{3}$  and an excess of sodium iodide and olefin were heated in refluxing benzene, but addition of DME to dissolve the sodium iodide did lead to formation of the desired products, albeit in low yield. Thus a reaction of trifluoromethylmercuric trifluoro-acetate with 3 molar equiv of NaI in the presence of allyltrimethylsilane in DME at reflux gave the expected cyclopropane product in 24% yield. The  $CF_{3}HgO_{2}CCF_{3}/NaI$  reaction carried out in DME in the presence of cyclohexene resulted in formation of 7,7-diffuoronorcarane, but only in 16% yield.

The reaction of trifluoromethylmercuric chloride with sodium iodide in DME in the presence of cyclohexene gave only a trace amount of 7,7-difluoronorcarane during a 24-hr reflux period. Initially, a white solid was deposited. Gradually this solid dissolved and was replaced by a greenish, oily lower layer. At the end of the heating period a two-layer system was present. The upper layer was light yellow, while the lower layer was green-gray. A trap-to-trap distillation in vacuo gave a clear, colorless distillate which contained only a trace amount of the desired norcarane derivative. Similar behavior was observed with trifluoromethylmercuric bromide. The results with CF<sub>3</sub>-HgCl and CF<sub>3</sub>HgBr were unexpected in view of the successful reactions with CF<sub>3</sub>HgI. It had been expected that both would react with iodide ion to give  $CF_{3}HgI$ , analogous to known RHgX + NaI reactions,<sup>23</sup> and that the latter would then give  $CF_2$  on further reaction with sodium iodide.

This unexpected behavior of  $CF_3HgCl$  and  $CF_3HgBr$ may find an explanation in the ability of RHgX compounds to form anionic complexes of type  $[RHgX_2]^$ and  $[RHgX_3]^{2-}$ . In particular, evidence for such complexes already has been cited by Emeléus and Lagowski in the case of the trifluoromethylmercuric halides.<sup>24</sup> Conductometric titrations of  $CF_3HgBr$  with potassium iodide gave evidence for formation of the species  $CF_3$ - $HgBrI^-$  and  $CF_3HgBrI_2^{2-}$ , with KBr, for  $CF_3HgBr_3^{2-}$ , and salts of the  $CF_3HgI_3^{2-}$  anion with  $Cd(en)_2^{2+}$ ,  $Cu(en)_2^{2+}$  and  $Ni(en)_2^{2+}$  counterions were isolated.<sup>24</sup>

In view of this previous work, it is then not too surprising that CF<sub>3</sub>HgCl and CF<sub>3</sub>HgBr do not transfer CF<sub>2</sub> on being treated with an excess of sodium iodide. What is surprising is the successful CF<sub>2</sub> transfer chemistry of CF<sub>3</sub>HgI under similar conditions. One may assume that kinetic factors (*i.e.*, those which lead to CF<sub>3</sub><sup>-</sup> displacement with CF<sub>3</sub>HgI and very likely stable anionic complex formation with CF<sub>3</sub>HgCl and CF<sub>3</sub>-HgBr) play an important role in these reactions with iodide ion. This question should receive further experimental attention.

### Conclusion

This investigation has shown PhHgCF<sub>3</sub> to be an excellent  $CF_2$  precursor. It is a stable, crystalline solid which is easily prepared and which releases  $CF_2$  under mild, nonbasic reaction conditions to give, on reaction

with olefins, *gem*-diffuorocyclopropanes in high yield. Its availability should facilitate further development of the chemistry of diffuorocarbene.

### **Experimental Section**

General Comments .--- All reactions were carried out in flamedried glassware in an atomosphere of prepurified nitrogen. The 'standard'' apparatus consisted of a three-necked, round-bottomed flask of appropriate size equipped with a stirrer (magnetic or motor driven), a reflux condenser topped with a nitrogen inlet tube, and, when required, pressure-equalizing addition funnel and/or a thermometer. Infrared spectra were recorded using Perkin-Elmer 237B, 257, or 457A grating infrared spectrophotometers, <sup>1</sup>H nmr spectra using a Varian Associates T60 spectrometer. Unless otherwise specified, carbon tetrachloride was used as solvent. Chemical shifts are reported in parts per million downfield from TMS. Gas chromatography was used extensively in the analysis of reaction mixtures, determination of product yields, and isolation of samples of products. The sodium iodide used was pulverized and dried for 18-24 hr at 150° (0.1 mm). Benzene, toluene, and chlorobenzene were distilled from appropriate drying agents. The progress of the reactions was monitored by thin layer chromatographic analysis for starting mercurial.12

The preparation of phenyl(trifluoromethyl)mercury has been described.<sup>17,18</sup> A variation of the second procedure,<sup>18</sup> developed by Mr. G. J. Murphy, however, is preferable since it is more direct and is described in detail.<sup>25</sup>

A 200-ml, three-necked flask equipped with a magnetic stirring assembly, a pressure-equalizing addition funnel, and a reflux condenser topped with a nitrogen inlet tube was charged with 21.1 g (55.0 mmol) of  $CF_3HgO_2CCF_3$ , <sup>16</sup> 19.4 g (54.8 mmol) of diphenylmercury, and 100 ml of dry benzene. The resulting solution was stirred and heated at reflux for 1 hr. Subsequently, 50 ml of saturated aqueous ammonium chloride was added. A large amount of white solid was formed at the layer interface. The reaction mixture was cooled and filtered to remove 19.4 g of white powder, mp 255–258° (mostly PhHgCl). The organic layer was dried and evaporated at reduced pressure to give white crystalline solid. Recrystallization of the latter from hexane gave 13.85 g (73%) of PhHgCF<sub>3</sub>, mp 141–143°.

General Procedure for PhHgCF<sub>3</sub>/NaI/Olefin Reactions.—The standard apparatus was charged (under nitrogen) with 1 molar equiv of phenyl(trifluoromethyl)mercury, 2.5–3.0 molar equiv of well-dried sodium iodide, and 3.0 molar equiv of the dried olefin. An appropriate amount (about 15-20 ml per 10 mmol of PhHgCF<sub>3</sub>) of benzene was distilled directly into the reaction flask from sodium benzophenone ketyl. The reaction mixture then was stirred and heated at reflux under nitrogen for 12–18 hr (except as noted). The reaction mixture was allowed to cool to room temperature, and the solids (PhHgI, NaF, and unreacted NaI) were filtered. The filtrate was trap to trap distilled at reduced pressure into a receiver at -78 to  $-196^\circ$ . The distillate was analyzed by glc and samples for spectroscopic, physical, and analytical characterization were isolated by glc. Details of specific reactions follow.

Glc analysis of reaction mixtures was accomplished using a 6-ft commercial aluminum 20% Dow Corning DC 200 silicone oil on Chromosorb W column. Many of the gem-difluorocyclopropanes reported here had been prepared during the course of our earlier study of the Me<sub>3</sub>SnCF<sub>3</sub>/NaI system,<sup>10b</sup> and spectra and in some cases authentic samples were available for comparison.

Cyclohexene (15.8 mmol), PhHgCF<sub>3</sub> (5.5 mmol), and NaI (12.5 mmol) in 30 ml of benzene at reflux for 15 hr gave 7,7-difluoronorcarane<sup>10b</sup> in 83% yield. The solids were Soxhlet extracted with benzene to give 1.95 g (70%) of slightly impure PhHgI, mp 274-278°. A reaction of 5.0 mmol of PhHgCF<sub>3</sub>, 12.5 mmol of NaI, and 10 ml of cyclohexene (no benzene), 15 hr at reflux, gave 7,7-difluoronorcarane in 81% yield.

Cyclooctene (60 mmol), PhHgCF<sub>3</sub> (20 mmol), and NaI (50 mmol) in 50 ml of benzene at reflux for 15 hr gave 9,9-difluorobicyclo[6.1.0]nonane,  $n^{25}D$  1.4338, in 83% yield. Anal. Calcd for C<sub>9</sub>H<sub>14</sub>F<sub>2</sub>: C, 67.47; H, 8.81. Found: C,

Anal. Calcd for  $C_{\theta}H_{14}F_{2}$ : C, 67.47; H, 8.81. Found: C, 67.56; H, 8.80.

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<sup>(25)</sup> Added in proof, November 1972.

Ir (liquid film): 3010 (m), 2920 (s), 2860 (s), 2790 (w), 1480 (s), 1455 (s), 1450 (s), 1375 (w), 1370 (m), 1350 (m), 1335 (m), 1305 (s), 1290 (s), 1265 (s), 1225 (s), 1210 (s), 1145 (m), 1175-1165 (s), 1085 (m), 1075 (w), 1040 (m) 1025 (m), 1005 (s), 965 (s), 955 (s), 885 (w), 865 (s), 845 (m), 805 (m), 775 (m), 750 (m), 675 (m), 645 cm<sup>-1</sup> (m).

cis-3-Hexene (60 mmol) (Chemical Samples Co., 98% isomerically pure), PhHgCF<sub>8</sub> (20 mmol), and NaI (50 mmol) in 50 ml of benzene at reflux for 15 hr gave 1,1-difluoro-cis-2,3-diethylcyclopropane,  $n^{25}$ D 1.3270, in 93% yield. Anal. Calcd for C<sub>7</sub>H<sub>12</sub>F<sub>2</sub>: C, 62.67; H, 9.02. Found:

62.57; H, 9.20. The glc retention time, 15.5 min, on a 20% SE-30 on Chromosorb W column at 57° and 15 psi helium (MIT isothermal unit) was different from that of the difluorocyclopropane derived from trans-3-hexene, 12.8 min.

Ir (liquid film): 3020 (m), 2980 (s), 2940 (s), 2880 (s), 2740 (m), 1480 (s), 1470 (s), 1380 (m), 1365 (m), 1340 (m), 1290 (s), 1270 (s), 1200 (s), 1160 (m), 1140 (m), 1110 (m), 1085 (m), 1040 (m), 1020 (m), 1000 (m), 990 (m), 960 (m), 940 (s), 900 (s), 820 (s), 790 (s), 750 (m), 700 (s), 680 (m), 640 cm<sup>-1</sup> (m).

trans-3-Hexene (60 mmol) (Chemical Samples Co., 98% isomerically pure), PhHgCF<sub>3</sub> (20 mmol), and NaI (50 mmol) in 50 ml of benzene at 60-70° for 48 hr gave 1,1-difluoro-trans-2,3diethylcyclopropane,  $n^{25}$  D 1.3670, in 94% yield. Anal. Calcd for C<sub>7</sub>H<sub>12</sub>F<sub>2</sub>: C, 62.67; H, 9.02. Found: C,

62.82; H, 9.00.

Ir (liquid film): 3150 (w), 3080 (s), 3040 (s), 2980 (s), 2740 (m), 1480 (s), 1460 (s), 1380 (m), 1360 (m), 1340 (m), 1260 (s), 1200 (s), 1150 (m), 1100 (w), 1085 (w), 1050 (m), 1020 (w), 1000 (w), 960 (m), 875 (s), 790 (s), 785 (s), 770 (m), 715 (s),  $680 (s), 670 (s), 650 \text{ cm}^{-1} (s).$ 

1-Heptene (15 mmol) (Chemical Samples Co.), PhHgCF<sub>3</sub> (5 mmol), and NaI (12.5 mmol) in 30 ml of benzene at reflux for 15 hr gave 1,1-difluoro-2-n-amylcyclopropane, n<sup>25</sup>D 1.3820 (lit.<sup>10b</sup> n<sup>25</sup>D 1.3813), in 70% yield.

Allyltrimethylsilane (20 mmol), PhHgCF<sub>3</sub> (7.5 mmol), and NaI (18.7 mmol) in 40 ml of benzene at reflux for 15 hr gave 1,1difluoro-2-(trimethylsilylmethyl)cyclopropane, n<sup>25</sup>D 1.3910 (lit.<sup>10b</sup>  $n^{25}$ D 1.3899), in 100% yield.

Vinyldimethylethylsilane (60 mmol), PhHgCF<sub>3</sub> (20 mmol), and NaI (50 mmol) in 50 ml of benzene at reflux for 15 hr gave 1,1-difluoro-2-(dimethylethylsilyl)cyclopropane,  $n^{25}{
m D}$  $1.\overline{3}960$ (lit.<sup>10b</sup> n<sup>25</sup>D 1.3962), in 44% yield.

Vinyltrimethylsilane (30 mmol), PhHgCF<sub>3</sub> (12 mmol), and NaI (30 mmol) in 30 ml of chlorobenzene at  $60^{\circ}$  for 48 hr and 90° for 12 hr gave 1,1-difluoro-2-(trimethylsilyl)cyclopropane, n<sup>25</sup>D 1.3822, in 53% yield.

Anal. Calcd for C<sub>6</sub>H<sub>12</sub>F<sub>2</sub>Si: C, 47.96; H, 8.05. Found: C, 48.11; H, 8.13.

Ir (liquid film): 3020 (w), 2960 (s), 2900 (m), 1460 (s), 1455 (s), 1365 (s), 1255 (s), 1180 (s), 1085 (s), 1040 (s), 1020 (s), 960 (m), 950 (m), 910 (s), 890 (s), 860-840 (s), 760 (m), 710 (m), 670 cm<sup>-1</sup> (m). Nmr:  $\delta 0.17$  (s, 9 H, Me<sub>3</sub>Si) and 1.0 ppm (m, 3 H, eyclopropyl H).

**2,5-Dihydrofuran** (30 mmol), PhHgCF<sub>8</sub> (10 mmol), and NaI (30 mmol) in 30 ml of benzene at 70° for 48 hr gave 3-oxa-6,6difluorobicyclo [3.1.0] hexane, n<sup>25</sup>D 1.3944 (lit.<sup>10b</sup> n<sup>25</sup>D 1.3942), in 67% yield.

Vinyl acetate (30 mmol), PhHgCF<sub>3</sub> (10 mmol), and NaI (30 mmol) in 30 ml of benzene ar reflux for 15 hr gave 1,1-difluoro-2acetoxycyclopropane in 84% yield. No other product was detected in the gas chromatogram.

Acrylonitrile (30 mmol), PhHgCF<sub>8</sub> (10 mmol), and NaI (30 mmol) in 30 ml of toluene (benzene interfered in product isolation) at 90° for 20 hr gave 1,1-difluoro-2-cyanocyclopropane, n<sup>25</sup>D 1.3710, in 26% yield.

Anal. Caled for C4H3NF2: C, 46.61; H, 3.00. Found: C, 46.47; H 3.48.

Ir (liquid film): 3110 (m), 3055 (m), 3020 (m), 2265 (s), 1470 (s), 1385 (s), 1310 (s), 1240 (vs), 1100 (w), 1080 (m), 1055 (m), 1000 (s), 950 (s), 915 (m), 820 (w), 725 (m), 650 cm<sup>-1</sup> (m).

Trichloroethylene (40 ml, used as solvent), PhHgCF<sub>3</sub> (20 mmol), and NaI (50 mmol) at reflux for 15 hr gave 2,2-difluoro-1,1,3-trichlorocyclopropane,  $n^{25}$ D 1.4227, in 72% yield.

Anal. Calcd for C3HCl3F2: C, 19.86; H, 0.56. Found: C, 19.76; H, 0.62.

Ir (liquid film): 3045 (m), 1420 (s), 1400 (m), 1275 (s), 1200 (s), 1045 (s), 1035 (s), 990 (s), 905 (s), 860 (s), 810 (s), 740 (w),  $690 \text{ cm}^{-1}(s).$ 

<sup>1</sup>H nmr:  $\delta$  3.79 ppm [d, J(HF cis) = 11 Hz]. <sup>19</sup>F nmr (in CCl<sub>4</sub>, downfield from 1,1,2,2-tetrafluoro-3,3,4,4-tetrachlorocyclobutane):  $\delta$  18.1 [d, J(FF) = 157 Hz] and 29.7 ppm [d, J(FF) = 157 Hz].

Reaction of Phenyl(trifluoromethyl)mercury with Cyclooctene in the Presence of Tri-n-butyltin Bromide.-The standard apparatus was charged with 4.15 g (12 mmol) of the mercurial, 13.3 g (36 mmol) of tri-n-butyltin bromide [prepared by reaction of bis(tri-n-butyltin) oxide and hydrobromic acid], and 20 ml of dry cyclooctene. The reaction mixture was heated at reflux, with stirring, under nitrogen for 7 days, until the indicated that the mercury reagent had been consumed. The very viscous reaction mixture was filtered from 6.80 g of solid, which was washed with benzene. The filtrate was poured into 50 ml of 10% potassium fluoride in 1:1 water-ethanol and then 100 ml of benzene was added. The mixture was shaken vigorously. The resulting gelatinous mass of solid was rendered filterable through the addition of 50 ml of acetone and further shaking. Filtration gave 8.60 g of tri-n-butyltin fluoride. The filtrate was dried and concentrated by distillation at atmospheric pressure. The residue was trap-to-trap distilled at 0.05 mm. Glc analysis of the filtrate showed the presence of 9,9-difluorobicyclo[6.1.0]nonane in 56% yield. An isolated sample had  $n^{25}$ D 1.4339 and an ir spectrum which was identical with that of an authentic sample.

A similar reaction carried out with 10 mmol of PhHgCF<sub>3</sub>, 30 mmol of tri-n-butyltin chloride (M & T Chemicals, Inc.), and 25 ml of cyclooctene (reflux for 12 days) gave 9,9-difluorobicyclo-[6.1.0] nonane in 55% yield. This product was obtained in 37% yield when 12 mmol of PhHgCF<sub>3</sub>, 36 mmol of triphenyltin bromide, and 20 ml of cyclooctene were heated at reflux under nitrogen for 10 days.

When 5 mmol (1.73 g) of PhHgCF<sub>3</sub> in 25 ml of cyclooctene was heated at reflux under nitrogen for 10 days, no 9,9-diffuorobi-cyclo[6.1.0]nonane was produced. Trap-to-trap distillation of the solution at 0.05 mm left a residue of 1.81 g of solid, mp 137-142°. Recrystallization from 3:1 hexane-chloroform gave 1.05 g of pure PhHgCF<sub>3</sub>, mp 140-142°. Glc examination of the distillate showed the expected product to be absent.

 $\label{eq:Reaction of Phenyl (trifluoromethyl) mercury with Trimethyl times and the trimethyl (trifluoromethyl) mercury with Trimethyl times and the tripluoromethyl (trifluoromethyl) mercury with Trimethyl times and the tripluoromethyl (trifluoromethyl) mercury with Trimethyl times and the tripluoromethyl mercury with Trimethyl mercury with Trimethyl times and the tripluoromethyl mercury with Trimethyl$ Bromide.-A solution of 20 mmol of PhHgCF3 and 60 mmol of trimethyltin bromide in 20 ml of dry chlorobenzene was heated under nitrogen at 130° for 4 days with stirring. Filtration removed 1.7 g of crude PhHgBr, which was purified by recrystallization from benzene to give material with mp 276-280°. The filtrate was trap to trap distilled at 0.05 mm, leaving a 0.1-g residue of PhHgCF<sub>3</sub> (identified by tlc). Examination of the distillate by glc (20% SE-30 on Chromosorb P at 110°) showed the presence of trimethyl(trifluoromethyl)tin. A sample was isolated by glc; its glc retention time and ir spectrum were in excellent agreement with those of authentic material.<sup>10b</sup>

A similar reaction was carried out between 10 mmol each of trimethyl(trifluoromethyl)tin and phenylmercuric bromide in 25 ml of chlorobenzene at 130° for 3 days. Filtration was followed by trap-to-trap distillation of the filtrate at 0.05 mm. The pot residue was crystallized from hexane to give a small amount of PhHgCF<sub>3</sub> (mp 140.5-144° and ir spectrum). Glc examination of the distillate showed trimethyltin bromide to be present (glc retention time, peak enhancement, and ir spectrum of an isolated sample)

Reactions of CF<sub>3</sub>HgX Compounds with Sodium Iodide in the Presence of Olefins. A. Trifluoromethylmercuric lodide.—The procedure described for PhHgCF<sub>3</sub>/NaI/olefin reactions was used in the reaction of 10 mmol of trifluoromethylmercuric iodide,<sup>18</sup> 30 mmol of sodium iodide, and 30 mmol of cyclohexene in 40 ml of benzene for 20 hr at reflux. During the course of the reaction, red mercuric iodide precipitated. The pink solids (8.05 g) were filtered and the filtrate was trap to trap distilled. Glc analysis established the presence of 7,7-diffuoronorcarane in 88% yield. An isolated sample had  $n^{25}$ D 1.4130 and an ir spectrum which agreed with that of an authentic sample.

A similar reaction of 9.7 mmol of CF<sub>3</sub>HgI and 30 mmol of NaI in 30 ml of benzene in the presence of 30 mmol of allyltrimethylsilane for 20 hr at reflux gave 1,1-difluoro-2-(trimethylsilyl-methyl)cyclopropane,  $n^{25}$ D 1.3890, in 78% yield.

Trifluoromethylmercuric Trifluoroacetate.-The В. same procedure was used in a reaction of 10 mmol of CF<sub>3</sub>HgO<sub>2</sub>CCF<sub>3</sub><sup>18</sup> and 40 mmol of NaI in the presence of 30 mmol of cyclohexene in a solvent mixture of 30 ml of benzene and 20 ml of DME (distilled successively from potassium and from lithium aluminum hydride). The NaI dissolved in DME was added dropwise to

## Allenes as Ground-State Carbenes

the hot mercurial/olefin/benzene solution over 30 min, and the reaction mixture was heated at reflux for an additional 2 hr. At the end of this time tlc showed that none of the starting mercury reagent was present. The cooled reaction mixture (a three-layer system) was trap to trap distilled. Glc analysis of the distillate showed the presence of 7,7-difluoronorcarane in 16% yield.

A similar reaction carried out in benzene at reflux (no DME) for 20 hr gave none of the expected norcarane derivative.

The reaction of 10 mmol of  $CF_8HgO_2CCF_8$  and 40 mmol of NaI in the presence of 30 ml of allyltrimethylsilane in 20 ml of benzene and 20 ml of DME, carried out using the procedure described above, gave 1,1-difluoro-2-(trimethylsilylmethyl)cyclo-propane in 24% yield.

C. Trifluoromethylmercuric Chloride.—A solution of 30 mmol of NaI in 20 ml of dry DME was added over a 30-min period to a stirred and heated solution of 5 mmol of CF<sub>8</sub>HgCl<sup>18</sup> and 30 mmol of cyclohexene in 10 ml of benzene. A white solid deposited as the NaI was added. This became gradually green and oily as the addition progressed and finally went into solution. The reaction was heated at reflux for 1 hr and then was cooled to room temperature. A two-layer system resulted. The upper

light yellow layer contained no 7,7-difluoronorcarane (by glc). Trap-to-trap distillation at 0.05 mm gave a water-white distillate which was shown by gle to contain only trace amounts of 7,7-difluoronorcarane. None of this product was present in a similar reaction mixture in which the solvent contained no DME.

Very similar behavior was observed with trifluoromethyl-mercuric bromide.  $^{18}$ 

**Registry No.**—Phenyl(trifluoromethyl)mercury, 24925-18-6; sodium iodide, 7681-82-5; trifluoromethylmercuric iodide, 421-11-4; trifluoromethylmercuric trifluoroacetate, 675-25-2; trifluoromethylmercuric chloride, 421-10-3; phenylmercuric iodide, 823-04-1.

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# Synthesis of (Fluoren-9-ylidene)(dibenzo[a,d]cyclohepten-5-ylidene)methane. Allenes as Ground-State Carbenes. I<sup>1</sup>

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The first representative of a novel class of allenes (3) was synthesized by dehydrogenation of the dihydro precursor 9, the latter compound being formed by the reaction of the phosphonium ylide 8 with the aldehyde 7. Interest in the allene was based on the possibility that polarization of the cumulene linkage, resulting from the special properties of the end groups, would impart divalent character to the central carbon. Spectroscopic data on the allene indicated that this expectation was only minimally realized in this tetraannelated representative.

Hine<sup>2</sup> has suggested that a stable carbene might be formed if the electron-deficient carbon is attached to an electron donor and an electron acceptor.

$$\ddot{\mathbf{X}}$$
— $\ddot{\mathbf{C}}$ — $\mathbf{Y}$   $\longleftrightarrow$   $\dot{\mathbf{X}}$ = $\mathbf{C}$ = $\mathbf{\overline{Y}}$ 

Using what might be considered an inversion of this concept, it occurred to us that allenes, appropriately substituted, might exhibit divalent character in the ground state. Two prototypical allenes (1 and 2) exemplify this concept.



Neither 1 nor 2, which are obviously closely related to the calicenes,<sup>3</sup> nor any of their derivatives are known compounds. In order, then, to examine the feasibility of this concept, the synthesis of the tetraannelated derivative, (fluoren-9-ylidene)(dibenzo[a,d]cyclohepten-5ylidene)methane (**3**), was undertaken. The representa-

(3) G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, Cambridge, England, 1969, p 76.



tive 3 of this novel class of allenes was chosen as the initial goal because of the added stability that annelation should impart to such a system and because of the commercial availability of certain suitable starting materials.

#### **Results and Discussion**

The synthesis of 3 was accomplished using the reaction sequence shown in Scheme I.

Synthesis of 9 was straightforward and proceeded in good yield. Reaction of 9 with DDQ in benzene provided a soluble fraction consisting of the allene and unreacted 9 and an insoluble fraction consisting of the hydroquinone and the tropylium salt 13. Based on the analogy of the reaction of tropylidene itself with DDQ,<sup>4</sup> it was initially assumed that the structure of the salt was 11. However, treatment of the salt with a variety of bases failed to convert it to the allene. Furthermore, the elemental analysis correlates substantially better with structure 13 than with 11.

The allene is a colorless solid, mp 242°, and its structure was established by several lines of evidence. Thus, the elemental analysis, molecular weight deter-

(4) D. H. Reid, M. Frazer, B. B. Molloy, H. A. S. Payne, and R. G. Sutherland, *Tetrahedron Lett.*, 530 (1961).

This work was supported by The Petroleum Research Fund, administered by The American Chemical Society, Grant 1339-G1.
 J. S. Hine, "Divalent Carbon," Ronald Press, New York, N. Y.,

<sup>(3)</sup> G. M. Badger, "Aromatic Character and Aromaticity," Cambridge