

## THE THERMAL DECOMPOSITION OF ORGANOMETALLIC HEAVY METAL TRIHALOACETATES IN THE PRESENCE OF OLEFINS\*

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### SUMMARY

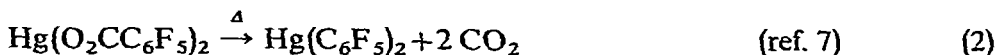
Thermolysis of trimethyltin and triphenyltin trichloroacetates in cyclooctene solution gave 9,9-dichlorobicyclo[6.1.0]nonane in moderate yield, and these reactions could also be carried out using smaller amounts of olefin in chlorobenzene or diglyme solution. 9,9-Dibromobicyclo[6.1.0]nonane was prepared in 35% yield in similar manner from triphenyltin tribromoacetate. A side reaction also gave benzene in the case of the triphenyltin compounds. The mechanism of these  $CX_2$  transfer reactions was not established, but a process involving decarboxylation and  $CX_2$  transfer from the  $R_3SnCX_3$  intermediate thus formed seems a reasonable possibility. The reaction of phenylmercuric chlorodifluoroacetate and trifluoroacetate with cyclooctene at the reflux temperature gave cyclooctyl chlorodifluoroacetate and trifluoroacetate, respectively, in high yield, as well as benzene and metallic mercury.

Much study has been devoted during the past five years to the trihalomethyl derivatives of metals and metalloids and their application as dihalocarbene transfer reagents<sup>2</sup>. Phenyl(trihalomethyl)mercury compounds in particular serve excellently as dihalocarbene sources<sup>3,4</sup>, and trichloromethyl derivatives of tin<sup>1</sup> and of lead<sup>5</sup> have been found to react with olefins to give *gem*-dichlorocyclopropanes. The preparation of trihalomethyl-metal compounds is, however, often time-consuming and difficult, and some of them, *e.g.*, those of tin, are very sensitive to atmospheric moisture. It was the purpose of this investigation to briefly survey a number of representative organometallic heavy metal trihaloacetates in order to find out if this class of stable and easily prepared compounds might serve as useful dihalocarbene transfer reagents. Such a possibility merited serious consideration, since the thermal decarboxylation of organometallic carboxylates is a reaction which has been and continues to be of preparative utility. Some recent examples are given in eqns. (1)–(3). The thermal decomposition of phenylmercuric trichloroacetate, on the other hand, has been reported to give phenylmercuric chloride; none of the expected phenyl-(trichloromethyl)mercury was isolated<sup>9</sup>.

\* Preliminary communication: ref. 1.

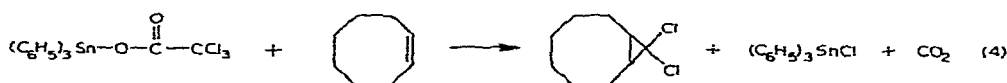
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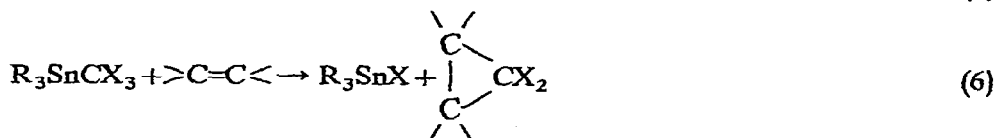
The heavy metal trihaloacetates which we have examined include derivatives of tin, lead, antimony and mercury:  $\text{Ph}_3\text{SnO}_2\text{CCX}_3$ ,  $\text{Me}_3\text{SnO}_2\text{CCX}_3$ ,  $\text{Ph}_3\text{PbO}_2\text{CCCl}_3$ ,  $\text{Ph}_2\text{SbO}_2\text{CCCl}_3$  and  $\text{PhHgO}_2\text{CCX}_3$ . Of these, only the tin compounds (where  $\text{X} = \text{Cl}$  and  $\text{Br}$ ) were found to transfer dihalocarbene to olefins to produce *gem*-dihalocyclopropanes.

Decarboxylation of triphenyltin trichloroacetate did not occur at *ca.* 80° in refluxing cyclohexene. However, when a cyclooctene solution of this tin compound was heated at reflux under nitrogen (b.p. of cyclooctene is 138°), a gas was evolved and subsequent gas-liquid partition chromatographic (GLC) analysis showed that 9,9-dichlorobicyclo[6.1.0]nonane had been formed in 56% yield. Thus the reaction shown in eqn. (4) had occurred. Another major product was benzene (13% yield).



which suggests the occurrence of a competing homolytic decomposition of starting tin compound. The same reaction was carried out in solvents—chlorobenzene and diethylene glycol dimethyl ether—using a cyclooctene/ $\text{Ph}_3\text{SnO}_2\text{CCCl}_3$  ratio of five; in each case 9,9-dichlorobicyclo[6.1.0]nonane was produced in about 40% yield. Refluxing a solution of triphenyltin trichloroacetate in  $\alpha$ -methylstyrene at 145° resulted in formation of 1,1-dichloro-2-methyl-2-phenylcyclopropane, but the yield of product was only 20%. Triphenyltin tribromoacetate reacted similarly, giving 9,9-dibromobicyclo[6.1.0]nonane in 35% yield when heated in cyclooctene at 147° for 20 h. Benzene (15%) was also formed. Trimethyltin trichloroacetate also decomposed in refluxing cyclooctene solution, and 9,9-dichlorobicyclo[6.1.0]nonane was produced in 53% yield. In this case, tetrachloroethylene (25%) was a by-product.

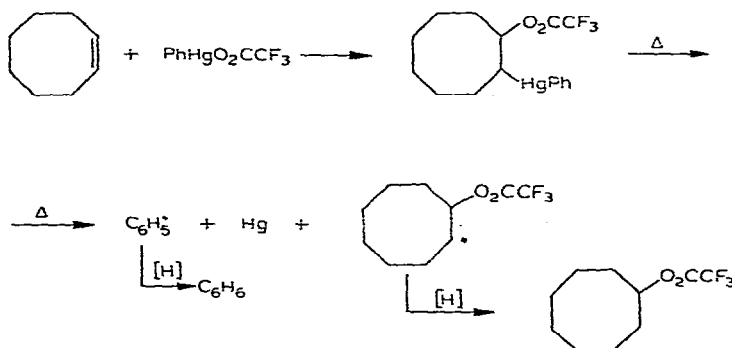
The high temperatures required for these reactions, together with the only moderate yields of product obtained, do not make this an attractive route to *gem*-dihalocyclopropanes. The mechanism of this reaction remains unknown as yet and in particular we do not know whether or not (trihalomethyl)tin compounds are involved as intermediates. Other work in these laboratories<sup>1</sup> has shown that  $(\text{CH}_3)_3\text{Sn}-\text{CCl}_3$  transfers  $\text{CCl}_2$  to cyclooctene under these conditions, so that in terms of known reactions, a decarboxylation- $\alpha$ -elimination sequence is a very reasonable possibility [eqns. (5) and (6)].



Attempts also were made to adapt the organotin ester route to provide a  $\text{CF}_2$  transfer system. However, triphenyltin trifluoroacetate did not decompose below  $200^\circ$ . Triphenyltin chlorodifluoroacetate decomposed slowly when heated in refluxing cyclooctene, but the only high-boiling product was produced in amounts insufficient to allow identification.

Extension of this study to the thermolysis of other heavy metal trihaloacetates was unsuccessful in terms of the hoped-for  $\text{CX}_2$  transfer system. Triphenyllead trichloroacetate and diphenylantimony trichloroacetate were decomposed to tars in refluxing cyclooctene and no 9,9-dichlorobicyclo[6.1.0]nonane was detected.

The behavior of phenylmercuric trihaloacetates when heated in cyclooctene differed markedly with the halogens present in the molecule. Phenylmercuric trichloroacetate, which decomposed smoothly to phenylmercuric chloride when heated as the solid, gave brown tar and only a trace of 9,9-dichlorobicyclo[6.1.0]nonane when heated in refluxing cyclooctene. The solid state decomposition of this compound appears to have caused some confusion concerning its melting point. A melting point of  $240^\circ$  has been reported for  $\text{PhHgO}_2\text{CCl}_3$ <sup>9</sup>. However, careful examination of this compound using a hot-stage microscope showed that decomposition occurred at  $139\text{--}140^\circ$ , with effervescence and collapse of the crystal structure, but without fusion. The new solid thus formed melted at about  $245^\circ$  (m.p. of  $\text{PhHgCl}$  is  $258\text{--}260^\circ$ ). Phenylmercuric trifluoroacetate and phenylmercuric chlorodifluoroacetate, on the other hand, reacted with cyclooctene at reflux to produce cyclooctyl trifluoroacetate (83%) and cyclooctyl chlorodifluoroacetate (86%), respectively, as well as benzene and metallic mercury. The esters obtained were identical in all respects to those prepared by reaction of cyclooctene with trifluoro- and chlorodifluoroacetic acids, respectively. Here again, the mechanism of this novel reaction is not known. We suggest as a reasonable possibility an initial mercuration reaction to give 2-(phenylmercuri)cyclooctyl trifluoro(or chlorodifluoro)acetate, followed by radical demercuration of the product, with subsequent abstraction of allylic hydrogens from cyclooctene by the radicals thus formed:



An attempt to prepare 2-(phenylmercuri)cyclooctyl trifluoroacetate by reaction of cyclooctene with phenylmercuric trifluoroacetate under milder conditions was not successful. In this connection one is reminded of the finding by Brown and Wirkkala<sup>10</sup> that aromatic mercuration by mercuric trifluoroacetate in trifluoroacetic acid proceeds very much more rapidly than mercuration with mercuric acetate in acetic acid.

Finally, triphenyltin chloroacetate and triphenyltin dichloroacetate were examined. Both decomposed on prolonged heating in cyclooctene, but no carbene adducts could be detected. The tarry residues were examined for the presence of (chloromethyl)triphenyltin and (dichloromethyl)triphenyltin, but no evidence for the formation of these decarboxylation products was obtained.

It is obvious from the results of this superficial investigation that the organotin trihaloacetate route to *gem*-dihalocyclopropanes offers no preparative advantages over the route based on phenyl(trihalomethyl)mercurials, and for this reason we contemplate no deeper probing into the exact nature of the  $R_3SnO_2CCX_3$  decomposition in solution and into the  $CX_2$  transfer process involving these compounds. The preparation of esters of trifluoroacetic acid and chlorodifluoroacetic acid by the reaction of phenylmercuric trifluoroacetate and chlorodifluoroacetate with olefins may have some advantages over the route involving direct addition of the acids to olefins<sup>11</sup>, since yields of ester are high and one may anticipate that the known acid-catalyzed carbon skeleton rearrangements and olefin dimerization reactions, which accompany the  $CF_3CO_2H$ /olefin reaction in some cases, would be avoided.

## EXPERIMENTAL

### *General comments*

All reactions of organometallic esters with olefins were carried out under an atmosphere of dry nitrogen or argon. Gas-liquid partition chromatography (GLC) was carried out using an F&M Model 700 gas chromatograph equipped with columns filled with 15% General Electric Co. SE-30 silicone rubber gum on Johns-Manville Chromosorb G (60-80 mesh) with a temperature program of 60-200° (10° per min), unless otherwise specified. Melting points are uncorrected. Analyses were performed by Dr. S. M. Nagy (MIT Microchemical Laboratory), the Galbraith Laboratories or the Schwarzkopf Microanalytical Laboratory.

### *Preparation of organometallic esters*

The following preparations are typical.

*Trimethyltin trifluoroacetate.* A mixture of 100 mmoles each of trimethyltin bromide and sodium trifluoroacetate in 60 ml of THF was heated at reflux, with stirring, for 4 h. Filtration of sodium bromide was followed by evaporation of the filtrate at reduced pressure. The white, crystalline residue was recrystallized from 2 : 1 benzene/heptane to give 16.9 g (61%) of product, m.p. (sealed tube) 84-85°.

*Phenylmercuric trichloroacetate.* Phenylmercuric chloride (57.5 mmoles) was stirred overnight with 3.6 g of KOH in 150 ml of ethanol. The mixture was poured into water and then filtered to give 17.0 g of crude phenylmercuric hydroxide. The latter was suspended in 100 ml of ethanol and 9.4 g of trichloroacetic acid in 50 ml of ethanol was added. The reaction mixture was heated briefly and filtered hot to remove a grey residue. Evaporation of the filtrate under reduced pressure gave 11.5 g of crude product. Recrystallization from benzene/pentane gave pure, white crystals of phenylmercuric trichloroacetate. On being heated on a hot-stage microscope this material was seen to effervesce, with collapse of the crystal structure, at 139-140°. The new solid melted at ~245°.

The organometallic esters prepared during this study are listed in Table 1.

Most were prepared by the reaction of the organometallic hydroxide or oxide with the appropriate acid.

TABLE I  
ORGANOMETALLIC TRIHALOMETHYLACETATES

Compound	M.p. (°C)	Analysis found (calcd.) (%)			
		Carbon	Hydrogen	Halogen	Metal
(CH <sub>3</sub> ) <sub>3</sub> SnO <sub>2</sub> CCCl <sub>3</sub>	174–175 <sup>a</sup>	18.11 (18.39)	2.58 (2.76)	33.04 (32.64)	
(CH <sub>3</sub> ) <sub>3</sub> SnO <sub>2</sub> CCF <sub>3</sub>	84–85	21.52 (21.71)	2.89 (3.25)	20.39 (20.52)	
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnO <sub>2</sub> CCCl <sub>3</sub>	88–89 <sup>b</sup>	47.0 (46.88)	3.45 (2.95)	19.70 (20.75)	
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnO <sub>2</sub> CCF <sub>2</sub> Cl	136–137.5	50.37 (50.10)	3.62 (3.15)		
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnO <sub>2</sub> CCF <sub>3</sub>	119–121	52.29 (51.88)	3.52 (3.24)		
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnO <sub>2</sub> CCBr <sub>3</sub>	135–137 <sup>c</sup>	37.16 (37.20)	2.19 (2.34)	36.95 (37.12)	
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnO <sub>2</sub> CCHCl <sub>2</sub>	176–178 <sup>d</sup>	50.19 (50.24)	3.55 (3.37)	15.52 (14.84)	
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnO <sub>2</sub> CCH <sub>2</sub> Cl	158–159	54.17 (54.14)	3.95 (3.83)	8.28 ( 7.99)	26.98 (26.76)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> PbO <sub>2</sub> CCCl <sub>3</sub>	174 <sup>e</sup>	39.67 (39.96)	2.69 (2.52)	18.08 (17.69)	34.19 (34.48)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SbO <sub>2</sub> CCCl <sub>3</sub>	126–127 <sup>f</sup>	38.38 (38.37)	2.34 (2.30)	24.45 (24.26)	
C <sub>6</sub> H <sub>5</sub> HgO <sub>2</sub> CCCl <sub>3</sub>	139–140 <sup>g</sup>	21.92 (21.83)	1.34 (1.14)		
C <sub>6</sub> H <sub>5</sub> HgO <sub>2</sub> CCF <sub>2</sub> Cl	75–77 <sup>h</sup>	22.99 (23.60)	0.99 (1.24)		
C <sub>6</sub> H <sub>5</sub> HgO <sub>2</sub> CCF <sub>3</sub>	108–112	25.17 (24.59)	1.59 (1.28)		

<sup>a</sup> Ref. 12 reports m.p. 175–176°. <sup>b</sup> Dec. 110°. <sup>c</sup> Dec. 150°. <sup>d</sup> Dec. 200°. <sup>e</sup> With effervescence and instant resolidification. <sup>f</sup> With effervescence. <sup>g</sup> With effervescence; new solid melts ca. 245°; *cf.* experimental section. <sup>h</sup> Effervescences above 110°.

#### Reaction of trimethyltin trichloroacetate with cyclooctene

The tin compound (29.8 mmoles) was suspended in 18 ml of the olefin and the resulting mixture was heated at reflux under nitrogen for 3 h. The dark reaction mixture was cooled and filtered to remove 2.1 g (22%) of crude, unconverted tin ester, m.p. 167–170°. The filtrate was trap-to-trap distilled at 0.1 mm (pot temperature to 60°). The clear distillate was analyzed by GLC (MIT isothermal unit, 15% SE-30 on Chromosorb W, 160° column temperature, 15 psi helium). The presence of tetrachloroethylene (25%, identified by means of its IR spectrum and GLC retention time) and 9,9-dichlorobicyclo[6.1.0]nonane (53%), as well as of trimethyltin chloride (yield not determined), was established. The cyclopropane product had  $n_D^{25}$  1.5033 (lit.<sup>13</sup> 1.5037) and its IR spectrum was identical with that of an authentic sample from a previous investigation<sup>13</sup>.

A similar reaction of 12.2 mmoles of trimethyltin trichloroacetate with 61.0 mmoles of cyclooctene in 60 ml of dry chlorobenzene at reflux for 8 h gave 9,9-dichlorobicyclo[6.1.0]nonane in 44% yield.

#### Reaction of triphenyltin trichloroacetate with cyclooctene

A slurry of 6.83 mmoles of the tin compound in cyclooctane was added slowly to 15 ml of refluxing cyclooctene under nitrogen. The reaction mixture was refluxed for 10 h. Trap-to-trap distillation at 0.05 mm followed. GLC analysis of the distillate showed that benzene (13%, based on available phenyl groups; identified by its IR spectrum and GLC retention time) and 9,9-dichlorobicyclo[6.1.0]nonane (56%) were the volatile products which had been formed.

Similar reactions were carried out between 15.7 mmoles of triphenyltin trichloroacetate and 78.5 mmoles of cyclooctene in 80 ml of chlorobenzene (5 h reflux) and 10.5 mmoles of the tin compound and 52.5 mmoles of the olefin in 20 ml of dry diglyme (5 h reflux). The yields of 9,9-dichlorobicyclo[6.1.0]nonane were 43% and 42%, respectively.

*Reaction of triphenyltin trichloroacetate with  $\alpha$ -methylstyrene*

A solution of 5 g of the tin compound in 15 ml of redistilled olefin was stirred at 145° for 8 h. Gas evolution began at about 130°. Trap-to-trap distillation at 0.1 mm left a brown solid residue. GLC analysis of the distillate showed the presence of benzene (20%, based on available phenyl groups) and 1,1-dichloro-2-methyl-2-phenylcyclopropane (20%, identified by comparison of its IR spectrum and GLC retention time with that of an authentic sample<sup>3</sup>.)

*Reaction of triphenyltin tribromoacetate with cyclooctene*

A solution of 5 g of the tin compound in 12.9 g of the olefin was heated at reflux for 20 h. Trap-to-trap distillation of the brown reaction mixture at 0.1 mm gave a colorless distillate and left a brown solid residue. GLC analysis of the distillate indicated the formation of benzene (5%, based on available phenyl groups) and 9,9-dibromobicyclo[6.1.0]nonane (35%). The latter was identified by means of its IR spectrum<sup>3</sup> and GLC retention time.

No reaction was observed when a solution of 5 g of triphenyltin tribromoacetate in 15 ml of cyclohexene was heated at reflux overnight.

*Reaction of phenylmercuric chlorodifluoroacetate with cyclooctene*

A solution of 9.82 mmoles of the mercury compound in 98.2 mmoles of the olefin was heated at reflux for 20 h, during which time the reaction mixture turned black. Trap-to-trap distillation of volatiles at 60–80° pot temperature and 0.1 mm left black tar and some metallic mercury. GLC analysis of the clear distillate (MIT isothermal unit; 15% SE-30 on Chromosorb G; 160°; 15 psi helium) showed the presence of benzene (42.4%) and cyclohexyl chlorodifluoroacetate (86.4%).  $n_D^{25}$  1.4290. (Found: C, 49.82; H, 6.31; Cl, 14.82; F, 15.58.  $C_{10}H_{15}ClF_2O_2$  calcd.: C, 49.90; H, 6.23; Cl, 14.72; F, 15.78%.) The IR spectrum (liquid film) showed bands at 2928 vs, 2860 s, 1760 vs, 1470 s, 1448 s, 1365 m, 1330 s, 1320 (sh), 1305 vs, 1255 w, 1230 w, 1165 vs, 1130 vs, 1110 (sh), 1075 (sh), 1040 m, 1025 w, 1000 (sh), 970 vs, 930 s, 900 m, 840 s, 800 m, 725 s  $cm^{-1}$ .

An authentic sample of cyclooctyl chlorodifluoroacetate was prepared by the reaction of 115.8 mmoles each of chlorodifluoroacetic acid and cyclooctene at room temperature for 70 h. Distillation of the mixture gave 60.4 mmoles of the ester (52%), b.p. 110°/18 mm,  $n_D^{25}$  1.4291. Its IR spectrum was identical with that of the product obtained above.

*Reaction of phenylmercuric trifluoroacetate with cyclooctene*

A solution of 12.8 mmoles of the mercury compound in 15 ml of cyclooctene was heated at reflux under nitrogen for 18 h. Trap-to-trap distillation at 0.1 mm left black tar and some metallic mercury. GLC analysis of the clear distillate showed the presence of benzene (59%) and cyclooctyl trifluoroacetate (83%). The latter was

identified by comparison of its GLC retention time and IR spectrum with those of an authentic sample.

Cyclooctyl trifluoroacetate (a sample for comparison) was prepared by adding 0.1 mole of cyclooctene slowly to 0.1 mole of trifluoroacetic acid at 70°<sup>11</sup>. The mixture was stirred overnight at 70°. Vacuum distillation gave the ester, and samples for analysis and IR spectrum determination were further purified by GLC. (Found: C, 53.57; H, 7.01. C<sub>10</sub>H<sub>15</sub>F<sub>3</sub>O<sub>2</sub> calcd.: C, 53.56; H, 6.75%.) The IR spectrum (pure liquid) showed bands at 2920 m, 2860 (sh), 1775 s, 1460 m, 1445 m, 1350 m, 1212 s, 1155 s, 1100 m, 1075 w, 1025 w, 930 m, 895 w, 865 w, 772 m, 725 w cm<sup>-1</sup>.

#### *Reaction of phenylmercuric trichloroacetate with cyclooctene*

A solution of 5 g of the mercury compound in 14 ml of cyclooctene was heated at reflux for 18 h. A very brisk effervescence was noted at 130°, with deposition of a solid. Trap-to-trap distillation at 0.1 mm left a brown tar and some metallic mercury. GLC analysis of the distillate showed the presence of benzene and a trace of a compound whose retention time matched that of 9,9-dichlorobicyclo[6.1.0]nonane.

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