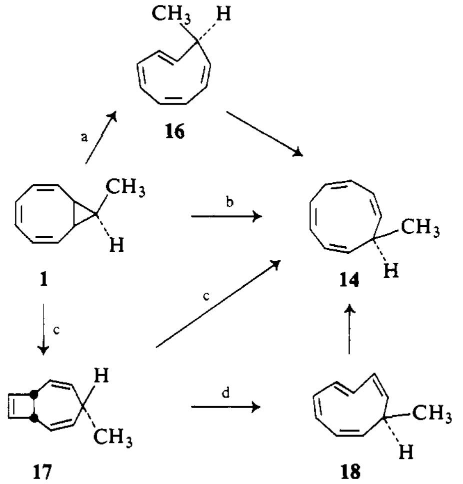
initial product, this reaction provides a convenient test for the intermediacy of **14** in the thermal transformations described above. When the anion **7** in tetrahydrofuran was treated with methyl iodide at *ca.* 25°, vpc[11] and nmr analyses of the products of the reaction indicated that the same five products were produced as in the thermolysis of **1** or **2** and that the two major components, again about 95% of the mixture, were **5** and **6** in a ratio of 87:13, respectively.

These results clearly indicate that **14** is an important intermediate in the thermolysis of **1** or **2** and that the main products of the reactions, **5** and **6**, arise from **14** through a $6\pi \rightarrow 4\pi 2\sigma$ disrotatory electrocyclic reaction. In addition, these results show that the thermolysis of *cis*-bicyclo[6.1.0]nona-2,4,6-trienes substituted at C_9 is not a stereospecific reaction, as it might have previously been considered.[7,8] That is, the predominance of one isomer, *i.e.*, **5** over **6**, is due only to the stereoselectivity in the $6\pi \rightarrow 4\pi 2\sigma$ ring closure of **14** to these latter products.

In view of these results we suggest that there are four possible mechanisms for the transformation of **1** to **14**. They are (a) a conrotatory $6\pi 2\sigma \rightarrow 8\pi$ ring opening of **1** to give **16** followed by thermal *trans* → *cis* double isomerization; (b) a direct ring opening of **1** to give **14**; (c) a concerted [3.3] sigmatropic rearrangement of **1** to give **17** followed either by a nonconcerted ring opening to **14**; or (d) a conrotatory ring opening to **18** followed by a *trans*–*cis* double bond isomerization.



In view of the facts that *trans*-bicyclo[6.1.0]nona-2,4,6-triene is stable to 100° and polymerizes at higher temperatures,[20] that *trans–cis* double bond isomerizations probably have higher activation energy barriers than are required here, and that a good estimate, based on known models, for the activation energy for the nonconcerted **17** → **14** conversion is *ca.* 20 kcal/mol,[21] we prefer the **1** → **17** → **14** → **5** + **6** mechanism. However, we defer further discussion of this topic until current experiments are concluded.

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New Functional Halomethylmercury Compounds and Halocarbenes

Sir:

The recent disclosure of the low-yield, photolytic production of chlorocarbethoxycarbene, $ClCCO_2Et$, from ethyl chlorodiazoacetate[1] prompts us to report our own work concerning the generation of chloro- and bromocarbomethoxycarbenes, as well as of chloro(trifluoromethyl)carbene, by thermolysis of an appropriate organomercury precursor.

Phenyl(dichlorocarbomethoxymethyl)mercury, mp (with slow decomposition) 140–144°, and phenyl(dibromocarbomethoxymethyl)mercury, mp 154–156° dec, were prepared in good yield by the reaction shown in eq 1,

$$\mathrm{PhHgCl + Me_3COK + HCX_2CO_2Me \xrightarrow[-60\ to\ -50°]{THF} PhHgCX_2CO_2Me + Me_3COH + KCl} \quad (1)$$

X = Cl, 75% yield
X = Br, 59% yield

using the general procedure we described recently for the synthesis of phenyl(trihalomethyl)mercurials in tetrahydrofuran medium.[2] Both mercurials appear to be good sources of the appropriate halocarbomethoxycarbene, although each is significantly more stable than its trihalomethyl analog, $PhHgCCl_3$ and $PhHgCBr_3$, respectively.

Transfer of $ClCCO_2Me$ was effected in 73% yield when 10 mmol of $PhHgCCl_2CO_2Me$, 38 mmol of cyclooctene, and 20 ml of chlorobenzene were heated at reflux under nitrogen for 11 days. (The progress of the reaction was followed by monitoring the consumption of the mercurial starting material by thin layer chromatography.[3]) The yield of phenylmercuric chloride was 91%. Both isomeric 9-chloro-9-carbomethoxybicyclo[6.1.0]nonanes were formed (in 1:3.5 ratio, in order of increasing retention time on a DC-200 silicone oil glpc column) (eq 2). The more abundant isomer had $n^{25}\mathrm{D}$ 1.4990. Phenyl(dibromocarbomethoxymethyl)mercury was found to be less stable thermally. In an analogous reaction with cyclooctene in chlorobenzene at reflux, phenylmercuric bromide was produced in 87% yield within 43 hr. The yield of the mixed 9-bromo-9-carbomethoxybicyclo[6.1.0]nonane isomers (bp 75–76° (0.03 mm); 1:2.3 ratio in order of increasing retention time on a silicone oil column) was 50%.

9-Chloro-9-carbomethoxybicyclo[4.1.0]heptane was not obtained when $PhHgCCl_2CO_2Me$ was treated with anhy-

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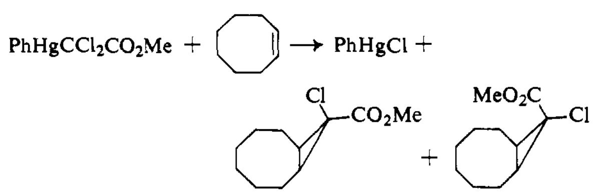

(2)

drous sodium iodide in 1,2-dimethoxyethane (DME)[4] in the presence of cyclohexene, presumably because of complicating side reactions of the $MeO_2CCl_2^-$ intermediate with C=O groups in the starting material and in any cyclopropane product that might have been produced.

Organomercury systems which serve well in the transfer of CF_3CCl also have been prepared (eq 3). Thermolysis

$$PhHgCl + Me_3COK + CF_3CXYH \xrightarrow[-10\text{ to }0^\circ]{THF} PhHgCXYCF_3 + Me_3COH + KCl \quad (3)$$

X = Y = Cl, 75% yield, mp 146–148.5°
X = Cl; Y = Br, 86% yield, mp 141–143°

of $PhHgCCl_2CF_3$ in the presence of cyclooctene (threefold excess) in chlorobenzene at 160° in a bomb tube did not proceed in high conversion during 6.5 days; phenylmercuric chloride was formed in only 25% yield. Glpc analysis of the trap-to-trap distilled filtrate indicated the formation of the *anti* and *syn* isomers of 9-chloro-9-trifluoromethylbicyclo[6.1.0]nonane in a total yield of 11%. Since phenyl(bromodichloromethyl)mercury decomposes so much more readily under comparable conditions than phenyl(trichloromethyl)mercury and hence is a much more effective CCl_2 precursor,[5] the mercurial $PhHgCClBrCF_3$ was prepared. As expected, it was much less stable and was almost completely decomposed (giving PhHgBr in 82% yield) on being heated in cyclooctene solution at reflux for 5.5 days. The 9-chloro-9-trifluoromethylbicyclo[6.1.0]nonane isomer to be eluted first upon glpc analysis using a DC-200 silicone oil column (n^{25}D 1.4371) was formed in 64% yield; the other isomer, n^{25}D 1.4439, was produced in 10% yield. In addition, a third product, present in 5% yield, was identified as 9-bromo-9-trifluoromethylbicyclo[6.1.0]nonane, n^{25}D 1.4571. Since the starting halocarbon used in the preparation of phenyl(1-bromo-1-chloro-2,2,2-trifluoroethyl)mercury, $CF_3CClBrH$ ("Fluothane," a product of the Ayerst Laboratories), was 99.9% pure by glpc (*i.e.*, free of CF_3CBr_2H), the formation of the CF_3CBr–cyclooctene adduct in 5% yield possibly represents a minor side reaction in which CF_3CBr and phenylmercuric chloride are produced. Such lack of specificity is not too surprising in view of the higher reaction temperature used. A similar lack of specificity was observed in the reaction of this mercurial with triethylsilane (eq 4).

$$PhHgCClBrCF_3 + Et_3SiH \xrightarrow[reflux]{PhCl} \underset{(51\%)}{Et_3SiCHClCF_3} + \underset{(4\%)}{Et_3SiCHBrCF_3} \quad (4)$$

Sodium iodide in DME was found to displace the $CF_3CCl_2^-$ anion from mercury. However, the anion decomposed with β elimination of fluoride ion, forming 1,1-dichloro-2,2-difluoroethylene, rather than *via* α elimination of chloride ion to give CF_3CCl (eq 5), in agreement with the previous work by Hine.[6] This experiment thus

$$PhHgCCl_2CF_3 + Na^+I^- \xrightarrow{DME} PhHgI + Na^+CCl_2CF_3^- \rightarrow NaF + CCl_2{=}CF_2 \quad (5)$$

provides further proof that *thermal* carbene extrusion from phenyl(polyhalomethyl)mercury compounds does not proceed by way of polyhalomethyl anion intermediates.

The present results, as well as earlier studies,[7,8] suggest that further research on the organomercury route to functional carbenes will be fruitful and that much new and useful carbene chemistry can be developed *via* this organometallic approach. We are actively pursuing further studies in this area.

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Reaction of Xenon Difluoride with Benzene[1]

Sir:

A variety of methods for selectively halogenating aromatic compounds are currently available. For fluorination, however, the picture is less satisfactory. The direct fluorination of benzene with fluorine gas[2] or cobaltic fluoride[3] yields only a mixture of nonaromatic fluorocarbons and tar. Ellis and Musgrave[4] have found that the primary process in the reaction of benzene and ClF_3C in CCl_4 in the presence of CoF_2 is one of substitution to give fluorobenzene and chlorobenzene in 26.6 and 58.5% yields, respectively. Addition compounds, biphenyls, and tar were also found. Fluorination of substituted benzenes by this method gave products consistent with an electrophilic mechanism.[5] CF_3OF has been found to react with salicylic acid to give, presumably by electrophilic substitution, 3- and 5-fluorosalicylic acids.[6]

We wish to report that xenon difluoride reacts with

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