Halomethyl–Metal Compounds. XLV. Organomercury CF_3CCl Transfer Reagents: $PhHgCCl_2CF_3$ and $PhHgCClBrCF_3$[1,2]

Dietmar Seyferth* and David C. Mueller[3]

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

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Abstract: The organomercury compounds $PhHgCCl_2CF_3$ and $PhHgCClBrCF_3$ have been prepared and evaluated as possible CF_3CCl transfer reagents. The former is too stable, even at 160°, to be a useful CF_3CCl source. $PhHgCClBrCF_3$, on the other hand, serves well in CF_3CCl transfer reactions at 130–140° to olefins and to silicon hydrides. Thus the reaction of $PhHgCClBrCF_3$ with cyclooctene (138° for 5.5 days) gave a mixture of both isomers of 9-chloro-9-trifluoromethylbicyclo[6.1.0]nonane in 74% yield, together with a small amount of 7-bromo-7-trifluoromethylbicyclo[6.1.0]nonane (5%). Reactions of this mercury reagent with cyclohexene, allyltrimethylsilane, tetramethylethylene, trimethylethylene, and *cis-* and *trans-*2-butene also are described. Product instability at the high reaction temperatures can be a problem (*e.g.*, the case of allyltrimethylsilane). Reaction of $PhHgCClBrCF_3$ with triethylsilane (*ca.* 130°, 6 days) gave $Et_3SiCHClCF_3$ in 52% yield, while reaction of this mercurial with triphenylphosphine in the presence of benzaldehyde gave the expected $PhCH{=}C(Cl)CF_3$ (38%). Sodium iodide in 1,2-dimethoxyethane displaced the CF_3CClX^- (X = Cl and Br) anions from $PhHgCCl_2CF_3$ and $PhHgCClBrCF_3$, respectively. These lost fluoride ion to give $CCl_2{=}CF_2$ and $CClBr{=}CF_2$, respectively. No CF_3CCl transfer to cyclohexene occurred under these conditions.

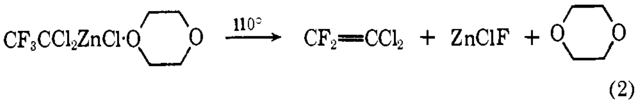
Our recent interest in organometallic routes to fluorine-containing carbenes[4] (*e.g.*, $PhHgCCl_2F \rightarrow CClF$,[5] $PhHgCF_3$–NaI → CF_2,[6] and Me_3SnCF_3–NaI → CF_2[7]) has prompted us to consider a similar method for the generation of trifluoromethyl-substituted carbenes. Various carbenes of this type have been described previously: CF_3CH *via* CF_3CHN_2,[8] CF_3CCN *via* $CF_3(CN)CN_2$,[9] $(CF_3)_2C$ *via* the diazoalkane and the diazirine.[10] However, carbenes of type CF_3CX (X = F, Cl, Br) have not been described and it was to the generation of CF_3CCl (or of a CF_3CCl "carbenoid") that we decided to devote our attention.

An organometallic reagent of type $MCXClCF_3$ (X = Cl or Br) would be required, and in view of our previous success with the application of phenyl(trihalomethyl)mercury compounds as dihalocarbene precursors,[11] the mercury compounds $PhHgCCl_2CF_3$ and $PhHgCClBrCF_3$ seemed the most promising.

However, it was by no means clear that CF_3CCl extrusion from these compounds (eq 1a) would be the preferred mode of decomposition since a β-elimination process (eq 1b) also was possible. In this connection, it may be noted that the decomposition of a CF_3CCl_2–zinc compound proceeded in the latter sense (eq 2).[12]

$$PhHgCXClCF_3 \rightarrow PhHgX + CF_3CCl \qquad (1a)$$

$$PhHgCXClCF_3 \rightarrow PhHgF + CXCl{=}CF_2 \qquad (1b)$$



(2)

Also, CF_3CCl_2Na, very likely an intermediate in the reaction of 2,2-dichloro-1,1,1-trifluoroethane with sodium methoxide, underwent fluoride ion elimination, giving $CF_2{=}CCl_2$.[13]

Some polyfluoroethylmercury compounds already were known, *e.g.*, $(CF_3CFCl)_2Hg$,[14] $(CF_3CCl_2)_2Hg$[15] (our desired substituent), $(CF_3CFH)_2Hg$,[14] $(CF_3CF_2)_2Hg$,[14,16] $(CF_3CFBr)_2Hg$,[17] and $CF_3CFClHgF$.[18] The addition of mercuric fluoride to the C=C bond of the respective fluoroolefin in anhydrous hydrogen fluoride or arsenic trifluoride served in their preparation. These compounds were found to be quite stable and their behavior on pyrolysis appears not to have been investigated. The compounds, all solids, melted without decomposition, $(CF_3CFCl)_2Hg$ at 93–95°, $(CF_3CCl_2)_2Hg$ at 180–185°, $CF_3CFClHgF$ at 118°. Thus there remained the questions concerning compounds of type $PhHgCXClCF_3$: (a) do they undergo α-elimination

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(2) Preliminary communication: D. Seyferth, D. C. Mueller, and R. L. Lambert, Jr., *ibid.*, **91**, 1562 (1969).

(3) National Science Foundation Graduate Fellow, 1967–1970.

(4) D. Seyferth, Carbene Symposium sponsored by the Divisions of Fluorine Chemistry and Organic Chemistry, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 14–19, 1970 (review paper).

(5) D. Seyferth and K. V. Darragh, *J. Org. Chem.*, **35**, 1297 (1970).

(6) D. Seyferth, S. P. Hopper, and K. V. Darragh, *J. Amer. Chem. Soc.*, **91**, 6536 (1969).

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(14) C. G. Krespan, *J. Org. Chem.*, **25**, 105 (1960).

(15) P. E. Aldrich, E. G. Howard, W. J. Linn, W. J. Middleton, and W. H. Sharkey, *ibid.*, **28**, 184 (1963).

(16) J. Banus, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 3041 (1950).

(17) P. Tarrant and D. E. O'Connor, *J. Org. Chem.*, **29**, 2012 (1964).

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of PhHgX or β-elimination of PhHgF on pyrolysis or reaction with a potential divalent carbon trap, and (b) can such decomposition or divalent carbon transfer be achieved at temperatures that are not so high as to preclude all application in synthesis?

In view of these uncertainties, an investigation of the chemistry of $PhHgCXClCF_3$ compounds seemed of considerable interest to us.

Results and Discussion

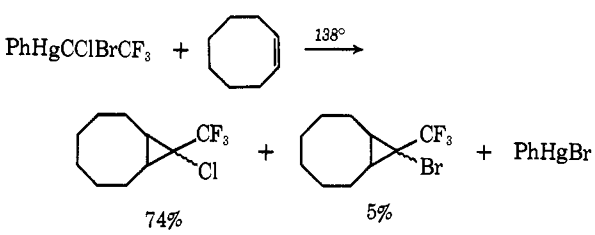
Synthesis and General Properties of the Organomercury Reagents. The two organomercury compounds, $PhHgCCl_2CF_3$ and $PhHgCClBrCF_3$, were prepared in excellent yield using a procedure (eq 3) analogous to that developed for the phenyl(trihalomethyl)mercury series.[19] Both compounds are stable, crystalline solids which do not decompose visibly at their melting points (X = Cl, 146–148.5°; X = Br, 141–143°) and even appear to be stable to rapid heating in capillary tubes to temperatures as high as 230°. Each mercurial reacted virtually quantitatively with anhydrous hydrogen chloride in benzene to give the respective 1,1-dihalo-2,2,2-trifluoroethylmercuric chloride, CF_3CCl_2HgCl (mp 181–182°) and $CF_3CClBrHgCl$ (mp 179–180°), both of which also are very stable thermally.

$$PhHgCl + Me_3COK + CF_3CXClH \xrightarrow{\text{THF, } -10 \text{ to } 0°} PhHgCXClCF_3 + Me_3COH + KCl \quad (3)$$

$$X = Cl,\ 75\%$$
$$X = Br,\ 86\%$$

The $PhHgCXClCF_3$ Compounds as Divalent Carbon Transfer Agents. In view of the high thermal stability of $PhHgCCl_2CF_3$ and $PhHgCClBrCF_3$, our experiments were carried out at higher temperatures. Phenyl-(1,1-dichloro-2,2,2-trifluoroethyl)mercury was too stable thermally to serve as a useful CF_3CCl transfer agent. Thus when this mercurial was heated with a large excess of cyclooctene in a sealed tube at 160° for 6.5 days, phenylmercuric chloride was obtained in only 25% yield. Both of the expected 9-chloro-9-trifluoromethylbicyclo[6.1.0]nonane isomers were formed, but they were present in only 11% yield. The stereochemistry of the isomers was not determined, but one was more abundant. The ratio of the isomer of shorter glc retention time (on both polar Carbowax 20M or General Electric Co. XE-60 and nonpolar dimethylsilicone columns) to that of longer retention time was 4.5.

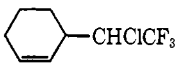
Since phenylmercuric bromide elimination usually is so much more rapid, under comparable conditions, than phenylmercuric chloride elimination (*cf.* $PhHgCCl_2Br$ *vs.* $PhHgCCl_3$),[11] it was expected that $PhHgCClBrCF_3$ would be a much more reactive CF_3CCl source than $PhHgCCl_2CF_3$. Such was found to be the case. When a cyclooctene solution of $PhHgCClBrCF_3$ was heated at reflux (138°) for 5.5 days, phenylmercuric bromide was formed in 82% yield and a 6.4 isomer ratio (as defined above) of the expected CF_3CCl adduct was formed in 74% yield (eq 4). A minor (5% yield) product also formed was 9-bromo-9-trifluoromethylbicyclo[6.1.0]nonane. Its formation was unexpected in view of the exclusive extrusion of CCl_2 from phenyl(bromodichloromethyl)mercury at 80°.[11,20] A similar lack of specificity had been noted previously in the reactions of PhHgCClBrH with triethylsilane at 130° [$\rightarrow Et_3SiCH_2Cl$ (72%) + Et_3SiCH_2Br (7%)][21] and of trimethyl(bromodichloromethyl)tin with cyclooctene at 140° (66% CCl_2 transfer, 5% CClBr transfer).[22] We suggest that the diminished specificity in these examples and in the present case is a consequence of the higher reaction temperatures employed. In terms of the transition state indicated for such α-elimination processes,[23] this explanation seems a reasonable one. A control experiment eliminated the possibility of halogen exchange between phenylmercuric bromide and 9-chloro-9-trifluoromethylbicyclo[6.1.0]nonane.



(4)

As eq 4 indicates, the $PhHgCXClCF_3$ reagents react with cyclooctene *via* an α-elimination process. β-Elimination, if it occurs at all, can only be a minor process. Having established that eq 1a is favored over eq 1b, we continued this study with further evaluation of $PhHgCClBrCF_3$ as a CF_3CCl transfer agent.

Phenyl(1-bromo-1-chloro-2,2,2-trifluoroethyl)mercury reacted with cyclohexene in benzene solution at 140° (sealed tube) to give both isomers (7:1 ratio, in order of increasing glc retention time on a Carbowax 20M column) of 7-chloro-7-trifluoromethylnorcarane in 41% total yield, together with a minor amount (2%) of 7-bromo-7-trifluoromethylnorcarane and another product (*ca.* 5% yield) tentatively identified as the allylic CH insertion product I. With allyltrimethylsilane, the yield of the expected 1-chloro-1-trifluoromethyl-2-trimethylsilylmethylcyclopropane was only 9% (135° for 6 days, no solvent). The phenylmercuric bromide yield was 72% and substantial (37%) amounts of trimethylchlorosilane and some benzene (19%) were present as well. The latter products indicate that the cyclopropane product was rather unstable to the reaction conditions (Scheme I). It may be noted that trimethylchlorosilane elimination from 1,1-dichloro-2-trimethylsilylmethylcyclopropane, catalyzed by zinc chloride, has been described.[24] In the present case, the mercury(II) halide derivatives present in the reaction mixture may have served as the mild Lewis acids generally required for such trimethylchlorosilane elimination. One thus may assume that the total yield of II was equal to the actually determined yield plus the yield of trimethylchlorosilane and benzene, *i.e.*, 65%. In contrast, heating $PhHgCClBrCF_3$ with trimethylvinylsilane under



I

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[19] D. Seyferth and R. L. Lambert, Jr., *J. Organometal. Chem.*, **16**, 21 (1969).

[20] The halocarbon used in the preparation of $PhHgCClBrCF_3$, "Fluothane" ($CHClBrCF_3$), a product of the Ayerst Laboratories, was examined carefully by gas–liquid partition chromatography and found to be completely free of CF_3CBr_2H and to show 99.9% purity.

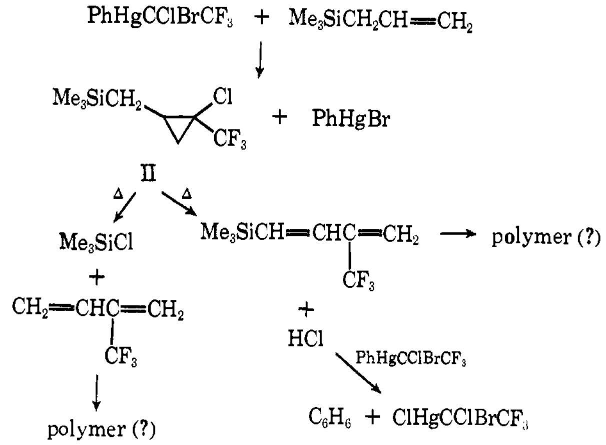
[21] D. Seyferth, S. B. Andrews, and H. D. Simmons, Jr., *J. Organometal. Chem.*, 17, 9 (1969).

[22] D. Seyferth and F. M. Armbrecht, Jr., *J. Amer. Chem. Soc.*, **91**, 2616 (1969).

[23] D. Seyferth, J. Y.-P. Mui, and R. Damrauer, *ibid.*, **90**, 6182 (1968).

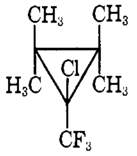
[24] D. Seyferth and T. F. Jula, *ibid.*, **90**, 2938 (1968).

Scheme I

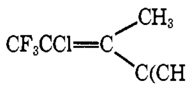


the same conditions gave phenylmercuric bromide in only 36% yield and no characterizable cyclopropane product was isolated.

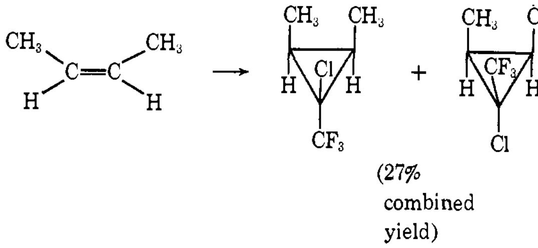
Reactions of $PhHgCClBrCF_3$ with several methyl-substituted ethylenes also were studied. With tetramethylethylene (54 hr at 130° in benzene), the expected cyclopropane (III) was produced in 58% yield. A second product (13%) also was present and this was identified tentatively as IV on the basis of its combustion analysis, mass, nmr, and ir spectra and a plausible mode of formation. Trimethylethylene reacted with the same mercury reagent (135°, 8 days) to give both isomers of the expected 1-chloro-2,2,3-trimethyl-1-trifluoromethylcyclopropane in 46% yield. Reactions with *cis*- and *trans*-2-butene were carried out (10 days, 135°) in order to obtain information concerning stereochemistry. While the yields of phenylmercuric bromide and cyclopropane were low in each case, the results did speak for CF_3CCl transfer to the olefins with retention of the original configuration about the C=C bond. In both reactions, which were carried out in chlorobenzene solution, the formation of some benzene was noted, an observation which again suggests that the products were not very stable to the reaction conditions.

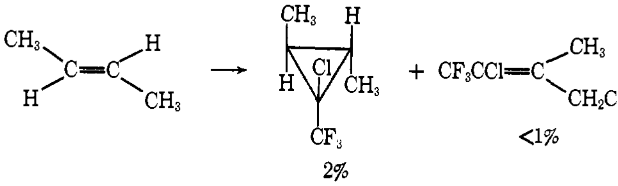


III



IV

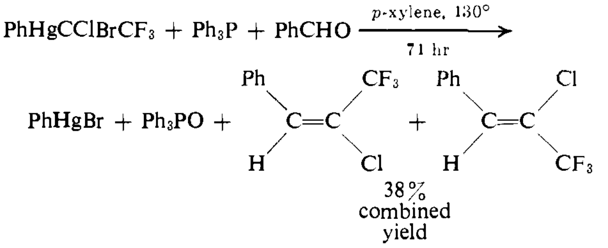




Finally, two other reactions characteristic of phenyl(trihalomethyl)mercurials were investigated. Insertion of CF_3CCl into the Si–H bond of triethylsilane (a particularly effective divalent carbon trap[25,26]) proceeded satisfactorily (eq 5). Again some CF_3CBr transfer occurred, since $Et_3SiCHBrCF_3$ also was present in 3% yield. Substantial amounts of triethylchlorosilane and lesser amounts of triethylbromosilane were formed as well, an indication that under the rather strenuous reaction conditions some reduction of Hg–halogen and C–halogen bonds by Et_3SiH had occurred.

$$\mathrm{PhHgCClBrCF_3 + Et_3SiH \xrightarrow{126\text{–}130^\circ,\ 6\ days} \underset{83\%}{PhHgBr} + \underset{52\%}{Et_3SiCHClCF_3}} \quad (5)$$

Another preparatively useful application of $PhHgCX_3$ compounds has been in the synthesis of $R_2C{=}CX_2$ type olefins from aldehydes and ketones.[27] Phenyl(1-bromo-1-chloro-2,2,2-trifluoroethyl)mercury is quite similar in its behavior, as its reaction with triphenylphosphine in the presence of benzaldehyde has shown (eq 6).



(6)

Although the foregoing reactions of $PhHgCClBrCF_3$ serve to demonstrate its general usefulness as a CF_3CCl reagent, the high reaction temperatures required and the resulting side reactions somewhat limit its applicability. It was thought, in analogy to the reactions of the phenyl(trihalomethyl)mercurials,[28] that reaction of $PhHgCCl_2CF_3$ and $PhHgCClBrCF_3$ with 1 equiv of sodium iodide in 1,2-dimethoxyethane (DME) in the presence of the olefinic substrate might provide an alternate route to thermal CF_3CCl transfer. In the case of $PhHgCX_3$ compounds, iodide ion was found to displace CX_3^- from mercury. The trihalomethyl anion then lost halide ion to give dihalocarbene (eq 7).[28] The present mercurials were indeed attacked at mercury by sodium iodide and the respective perhaloethyl anion was displaced. However, β-elimination of fluoride ion from the CF_3CClX^- intermediate was preferred over α-elimination of chloride or bromide ion, and the corresponding ethylenes were the only products obtained (eq 8). Such behavior was not unexpected in view of the previous work of Hine[13] mentioned earlier.

$$\mathrm{PhHgCX_3 + NaI \xrightarrow{DME} PhHgI + [NaCX_3] \longrightarrow {:}CX_2 + NaX} \quad (7)$$

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(25) (a) D. Seyfeth, J. M. Burlitch, H. Dertouzos, and H. D. Simmons, Jr., *J. Organometal. Chem.*, **7**, 405 (1967); (b) D. Seyferth, S. B. Andrews, and H. D. Simmons, Jr., *ibid.*, **17**, 9 (1969); (c) D. Seyferth, R. Damrauer, R. M. Turkel, and L. J. Todd, *ibid.*, **17**, 367 (1969); (d) D. Seyferth and S. P. Hopper, *ibid.*, **23**, 99 (1970).

(26) D. Seyferth, *Pure Appl. Chem.*, **23**, 391 (1970).

(27) D. Seyferth, J. K. Heeren, G. Singh, S. O. Grim, and W. B. Hughes, *J. Organometal. Chem.*, **5**, 267 (1966).

(28) D. Seyferth, M. E. Gordon, J. Y.-P. Mui, and J. M. Burlitch, *J. Amer. Chem. Soc.*, **89**, 959 (1967).

$$\begin{array}{l} \mathrm{PhHgCClXCF_3 + NaI} \xrightarrow{\text{DME, 80–85°}} \mathrm{PhHgI + [NaCClXCF_3]} \qquad (8) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\quad \mathrm{NaF + CF_2{=}CClX} \\ \qquad\qquad\qquad\qquad\qquad\quad \mathrm{X = Cl,\ 60\%} \\ \qquad\qquad\qquad\qquad\qquad\quad \mathrm{X = Br,\ 68\%} \end{array}$$

Some brief comments concerning the possible mechanism of thermal CF_3CCl transfer from $PhHgCClXCF_3$ are in order. First, a process involving CF_3CClX^- as an intermediate can be excluded. In the thermal reactions an α-elimination CF_3CCl transfer process is operative, but in the case of the sodium iodide reaction (a carbanion process[28]) it was fluoride ion which was lost and no CF_3CCl transfer was observed.

It is quite difficult to cite evidence either for or against a free carbene mechanism (of the type found for $PhHgCCl_2Br$[29]) or a direct organometallic transfer mechanism (as with $Hg(CH_2Br)_2$[30]). Stereochemistry does not distinguish between these possibilities if a singlet carbene is involved, retention being found in both cases.

Our yield *vs.* reaction time data for various olefin reactions are not of significance in view of the fact that sealed tube reactions often were involved whose progress could not be followed conveniently by tlc or glc. *If* a carbene is involved, the retention of stereochemistry, reasonably well documented in the case of *cis*-2-butene, would speak against a triplet species.[31] The formation of the observed olefinic by-products is explicable in terms of either triplet or singlet carbene intermediates or even in terms of a polar or free radical organometallic mechanism. In view of these uncertainties, further discussion of this point is not warranted.

Conclusions

This study has shown that $PhHgCClBrCF_3$ can be a useful CF_3CCl transfer agent that allows the preparation of compounds difficult to prepare by other routes, usually in fair to good yield. Optimum reaction conditions have not been defined and improvement in the yields of products should be possible. A limitation of this reaction is found in the relatively high temperatures and long reaction times required to effect it. Unfortunately many of the products formed by such CF_3CCl transfer have only limited stability under the reaction conditions and decompose to some extent during the reaction period.

Experimental Section

General Comments. All reactions using organomercury reagents were carried out under an atmosphere of dry nitrogen or argon unless otherwise specified in flame-dried glassware.

Nuclear magnetic resonance (nmr) spectra were recorded using a Varian Associates A-60 or T-60 high-resolution spectrometer. Chemical shifts are reported in δ units using either tetramethylsilane (δ 0.00) or chloroform (δ 7.27) as internal standards.

Infrared spectra were recorded using a Perkin-Elmer 237B, 337, or 257 grating infrared spectrometer. Intensities are reported as very strong (vs), strong (s), medium (m), weak (w), or shoulder (sh) with reference to the strongest band.

Gas-liquid partition chromatography was used routinely for yield determinations and for collection of analytical samples. Commercial stainless steel columns were employed with either an F & M Model 700, 720, or 5754 gas chromatograph. Several different columns were used: (A) 6 ft × 0.25 in. 10% DC-200 silicone oil (5754); (B) 4 ft × 0.25 in. 10% UC-W98 silicone rubber (5754); (C) 6 ft × 0.25 in. 10% Carbowax 20M (5754); (D) 6 ft × 0.25 in. 20% DC-200 silicone oil (700 or 720); (E) 6 ft × 0.25 in. 20% UC-W98 silicone rubber (700); (F) 6 ft × 0.25 in. 20% XE-60 silicone gum nitrile (700 or 720); (G) 12 ft × 0.25 in. 20% Carbowax 20M (700); (H) 6 ft × 0.25 in. 20% poly(phenyl ether) (700); (I) 6 ft × 0.25 in. 20% Carbowax 20M (700); (J) 6 ft × 0.25 in. 10% Apiezon L (5754); (K) 6 ft × 0.25 in. 20% Apiezon L (720); and (L) 4 ft × 0.25 in. 20% LAC 728 (700). All columns were packed on acid-washed, dimethylchlorosilane-treated Chromosorb W; a helium carrier gas flow rate of 40–60 ml/min was commonly employed. Internal standards were used in all yield analyses. Empirical response factors (RF) were determined separately using standard solutions according to the formula

$$\mathrm{RF} = \frac{\text{area (standard)}}{\text{mmole (standard)}}\,\frac{\text{mmole (product)}}{\text{area (product)}}$$

Peak areas were measured using an Ott planimeter.

Mass spectra were recorded using a Consolidated Electrodynamics Co. 130 or a Hitachi-Perkin Elmer RMU6D mass spectrometer.

Preparation of Phenyl(1,1-dichloro-2,2,2-trifluoroethyl)mercury. Into a 1-l. three-necked flask equipped with a paddle stirring unit and a Claisen adapter with a pentane thermometer and a nitrogen inlet tube was charged 31.31 g (0.10 mol) of phenylmercuric chloride and 19.90 g (0.130 mol) of 1,1,1-trifluoro-2,2-dichloroethane (Peninsular ChemResearch) in 280 ml of dry tetrahydrofuran (THF). The resulting slurry was cooled to 0° and 24 g (0.13 mol) of solid potassium *tert*-butoxide-mono-*tert*-butyl alcoholate[32,33] was added under nitrogen over a 6-min period using a solids addition funnel. During the course of the addition the solids dissolved and the solution became dark green in color. The reaction mixture was stirred for several minutes and then was transferred quickly to a one-necked flask. The volatile components were removed at reduced pressure (rotary evaporator), leaving a solid residue. The latter was extracted with 650 ml of dry benzene. The benzene extracts were filtered from some dark solid and evaporated to leave a white, semicrystalline solid. This was recrystallized from 5:1 *n*-hexane–chloroform in three crops to give 32.23 g (75%) of product as white needles, mp 139–145°.[34] A recrystallized sample, mp 146–148.5° (no visible decomposition below 230°), was characterized.

Anal. Calcd for $C_8H_5Cl_2F_3Hg$: C, 22.36; H, 1.17; Cl, 16.50; F, 13.26; Hg, 46.69. Found: C, 22.08; H, 1.29; Cl, 16.44; F, 13.26; Hg, 46.43.

Ir (KBr) showed 3062 w, 1582 w, 1483 w, 1432 m, 1269 m, 1250 vs, 1241 vs, 1193 sh, 1163 vs, 1022 w, 995 w, 902 w, 880 m, 841 w, 815 w, 781 vs, 732 vs, 687 s, 685 s, 547 w, and 444 cm^{-1} m.

Preparation of Phenyl(1-bromo-1-chloro-2,2,2-trifluoroethyl)-mercury. Analogous to the preceding experiment, a slurry of 31.31 g (0.10 mol) of phenylmercuric chloride and 22 ml (*ca.* 0.21 mol) of 2-bromo-2-chloro-1,1,1-trifluoroethane ("Fluothane," Ayerst Laboratories) in 300 ml of THF was prepared and cooled to 0°. Addition of 20.5 g of *tert*-BuOK-*tert*-BuOH (0.11 mol) over 15 min gave a clear solution which was evaporated to leave white solid. The latter was taken up in 750 ml of benzene and 50 ml of water. The organic layer was decanted through filter paper and evaporated to give a white, semicrystalline solid. Recrystallization from 3:1 *n*-hexane–chloroform gave 40.54 g (86%) of product, white needles, mp 140–144°. A recrystallized sample had mp 141–143° (no visible decomposition below 230°).

Anal. Calcd for $C_8H_5ClBrF_3Hg$: C, 20.27; H, 1.06. Found: C, 20.49; H, 1.07. (A 12.894-mg sample should give 10.213 mg of AgBr + AgCl; found: 10.240 mg.)

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(29) D. Seyferth, J. Y.-P. Mui, and J. M. Burlitch, *J. Amer. Chem. Soc.*, **89**, 4953 (1967).

(30) D. Seyferth, R. M. Turkel, M. A. Eisert, and L. J. Todd, *ibid.*, **91**, 5027 (1969).

(31) Typical triplet-type reactivity has been observed under certain reaction conditions for diazoalkane-derived CF_3CH[8] and $(CF_3)_2C$.[10]

(32) A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, **84**, 854 (1962).

(33) Commercially available unsolvated potassium *tert*-butoxide (MSA Corp.) which has been mixed with 1 molar equiv of dry *tert*-butyl alcohol in THF slurry serves equally well.

(34) A second crystalline form, heavy plates, mp 151–153°, was isolated in an analogous experiment carried out at a later date. The infrared spectra of the plates and needles were found to be identical.

Ir (KBr) showed 3050 w, 2982 w, 2100 w, 1960 w, 1945 w, 1880 w, 1860 w, 1805 w, 1570 m, 1475 s, 1425 s, 1325 w, 1304 w, 1252 vs, 1237 vs, 1193 sh, 1160 vs, 1080 w, 1060 w, 1021 m, 997 m, 904 w, 875 s, 841 w, 804 s, 744 vs, 731 vs, 689 vs, 676 vs, 545 w, 533 w, and 441 cm^{-1} vs.

Cleavage of the Phenyl(1,1-dihalo-2,2,2-trifluoroethyl)mercurials with Hydrogen Chloride. A 100-ml three-necked flask equipped with a magnetic stirring unit and gas inlet and exit tubes was charged with 6.44 g (15.0 mmol) of $PhHgCCl_2CF_3$ in 60 ml of dry benzene. Anhydrous hydrogen chloride was bubbled through the solution at a rapid rate for 25 min. A small amount of white solid precipitated. Evaporation of the volatile components at reduced pressure left a white solid residue which was crystallized from hexane to give 5.00 g (86%) of 1,1-dichloro-2,2,2-trifluoroethylmercuric chloride, long white needles, mp 179–183°. An analytical sample (from hexane) had mp 181–182°.

Anal. Calcd for $C_2Cl_3F_3Hg$: C, 6.19; Hg, 51.70. Found: C, 6.35; Hg, 51.90.

Cleavage of $PhHgCClBrCF_3$ with hydrogen chloride in similar fashion gave $CF_3CClBrHgCl$, mp 179–180°, in 91% yield (long white needles from hexane).

Anal. Calcd for $C_2Cl_2BrF_3Hg$: C, 5.55; Hg, 46.39. Found: C, 5.82; Hg, 46.09.

The ir spectrum of CF_3CCl_2HgCl (in KBr) showed bands at 1274 sh, 1240 vs, 1179 vs, 885 m, 815 sh, 797 s, 743 w, and 685 cm^{-1} s.

Reaction of $PhHgCClBrCF_3$ with Cyclooctene. A 100-ml three-necked flask equipped with a magnetic stirring unit and a condenser topped with a nitrogen inlet tube (standard apparatus for mercurial reactions) was charged with 10.88 g (23.0 mmol) of the mercury reagent and 30 ml of cyclooctene (Aldrich, freshly distilled from sodium). The reaction mixture was heated at reflux for 5.5 days. Phenylmercuric bromide, 6.73 g (82%), mp 278–281°, was filtered and the clear filtrate was trap-to-trap distilled at 0.03 mm (pot temperature to 70°), leaving 1.40 g of dark solid residue. Glc analysis of the distillate (column A, 140°) showed the presence of three components: (A) with retention time of 6.7 min, (B) with retention time of 7.4 min, and (C) with retention time of 9.8 min. The products were isolated by preparative glc (column G, 150°). (A) and (B) were identified as *syn*- and *anti*-9-chloro-9-trifluoromethylbicyclo[6.1.0]nonane (stereochemistry not assigned). The isomer with shorter retention time was present in 64% yield; it had $n^{25}D$ 1.4371; nmr (in CCl_4) δ 0.43–2.47 ppm.

Anal. Calcd for $C_{10}H_{14}ClF_3$: C, 52.98; H, 6.22; Cl, 15.64; F, 25.15. Found: C, 52.68; H, 6.58; Cl, 15.70; F, 25.65.

Ir (liquid film) showed 3000 sh, 2962 sh, 2925 vs, 2854 m, 1470 m, 1448 w, 1426 w, 1338 w, 1312 sh, 1300 vs, 1287 sh, 1263 w, 1241 w, 1235 w, 1180 sh, 1159 vs, 1109 w, 1070 m, 1056 sh, 1024 w, 945 w, 903 m, 852 w, 820 w, 783 w, 752 w, and 706 cm^{-1} m.

The other isomer, compound B, present in 10% yield, had $n^{25}D$ 1.4439.

Anal. Calcd for $C_{10}H_{14}ClF_3$: C, 52.98; H, 6.22. Found: C, 52.98; H, 6.27.

Mass spectrum (80 eV) showed *m/e* (relative intensity) 228, 226 (5.8, 17.5, M^+), 158, 156 (14.6, 43.1, $[M - HCF_3]^+$), 109 (24.1), 96 (66.4), 95 (23.4), 83 (26.3), 81 (93.4, CF_3C^+), 70 (36.5), 69 (27.0), 68 (41.6), 67 (66.4), 55 (100), 54 (51.8), 42 (27.0), 41 (96.4), 40 (41.3). The 228, 226 and 158, 156 pairs are in 1:3 ratio, confirming the presence of one chlorine atom.

Ir (liquid film) showed 2981 sh, 2925 vs, 2852 m, 2680 w, 1465 m, 1445 m, 1352 s, 1310 w, 1298 w, 1260 w, 1230 w, 1217 w, 1161 vs, 1147 vs, 1101 w, 1070 m, 1042 w, 947 w, 901 w, 878 m, 847 w, 820 w, 784 w, 757 w, 742 w, 717 w, and 703 cm^{-1} w.

The component with the longest retention time, compound C, present in 5% yield, $n^{25}D$ 1.4571, was identified as 9-bromo-9-trifluoromethylbicyclo[6.1.0]nonane.

Anal. Calcd for $C_{10}H_{14}BrF_3$: C, 44.30; H, 5.20. Found: C, 44.93; H, 5.17.

Mass spectrum (80 eV) showed *m/e* (relative intensity) 272, 270 (14.2, 14.9, M^+), 202, 200 (24.4, 26.0, $[M - HCF_3]^+$), 191 (29.1, $[M - Br]^+$), 149 (82.6), 135 (29.1), 96 (100), 81 (85.8), 68 (32.0), 67 (55.9), 55 (87.4), 54 (44.9), 41 (86.6), 38 (44.9). The infrared spectrum is very similar to that of compound A except for minor differences in the 700–900-cm^{-1} region. It may be noted that the 272, 270 and 202, 200 pairs in the mass spectrum have a 1:1 ratio, confirming the presence of one bromine atom.

Reaction of $PhHgCCl_2CF_3$ with Cyclooctene. A solution of 2.15 g (5.00 mmol) of the mercurial, 2.0 ml (*ca.* 15 mmol) of cyclooctene, and 5.0 ml of chlorobenzene was sealed in a 30-ml, heavy-walled bomb tube. The tube was shaken at 160° for 6.5 days during which time the originally clear, colorless solution darkened and white solid and finely divided mercury formed. The reaction mixture was filtered to give 0.390 g of phenylmercuric chloride contaminated with a minor quantity of metallic mercury. Its mp was 247–250° and the yield was *ca.* 25%. Work-up of the filtrate as described in the experiment above followed. Glc analysis (column C, 130°) showed that the two isomers of 9-chloro-9-trifluoromethylbicyclo[6.1.0]nonane, A and B, were present in 9 and 2% yield, respectively. Starting mercurial was recovered in 55% yield from the trap-to-trap distillation residue.

Reaction of $PhHgCClBrCF_3$ with Other Olefins. (a) Cyclohexene. The mercurial (10.0 mmol) and 5 ml of cyclohexene in 10 ml of benzene were sealed in a 30-ml bomb tube and shaken for 9 days at 140°. Phenylmercuric bromide was obtained in 70% yield. The usual work-up of the filtrate followed. Glc analysis (column G, 125°) and isolation of the products gave the following results. The major product had the shortest glc retention time and was identified as one of the isomers of 7-chloro-7-trifluoromethylnorcarane, $n^{25}D$ 1.4221, 36% yield.

Anal. Calcd for $C_8H_{10}ClF_3$: C, 48.37; H, 5.08. Found: C, 48.50; H, 5.01.

Nmr (in CCl_4) showed δ 0.93–2.33 m; ir (liquid film) 3025 w, 2948 vs, 2868 m, 1465 m, 1450 m, 1410 m, 1359 sh, 1346 m, 1298 vs, 1245 sh, 1160 vs, 1127 sh, 1096 s, 1084 sh, 1049 s, 1040 s, 1011 w, 978 w, 950 w, 922 m, 889 sh, 869 s, 849 s, 795 w, 763 w, 716 sh, 707 s, and 653 cm^{-1} w. The mass spectrum (80 eV) showed the molecular ion at *m/e* 200 and 198 in 1:3 ratio, indicating the presence of one chlorine atom.

The last of the three peaks to be eluted on glc was identified as one of the isomers of 7-bromo-7-trifluoromethylnorcarane (*ca.* 2% yield). Its infrared spectrum was very similar to that of the major product. Mass spectrum (80 eV) showed *m/e* 244, 242 (2.3, 2.3, M^+), 163 (25, $[M - Br]^+$), 78 (21), 68 (58), 55 (29), 43 (100). The low yield of this product precluded further characterization.

The second peak to be eluted on glc was found (column D, 110°) to contain three components: on the gas chromatogram a minor peak overlapped the leading edge of a major peak and the latter was followed by another major peak. Combustion analysis indicated that this mixture contained components which were isomeric with the major product.

Anal. Calcd for $C_8H_{10}ClF_3$: C, 48.37; H, 5.08. Found: C, 48.48; H, 4.91.

The last of the three components could be separated by glc. Its nmr spectrum showed only a multiplet at δ 1.52–2.75 ppm. Ir (liquid film) showed 3011 w, 2960 sh, 2940 s, 2900 sh, 2888 m, 2852 m, 1468 sh, 1444 m, 1386 sh, 1367 vs, 1331 sh, 1310 w, 1268 m, 1258 sh, 1205 s, 1174 sh, 1159 vs, 1136 sh, 1092 m, 1075 m, 1042 m, 1028 m, 985 w, 909 m, 860 m, 840 w, and 657 cm^{-1} w. Its yield could be estimated as 5%, and the available evidence suggests that it is the other 7-chloro-7-trifluoromethylnorcarane isomer.

The other major component of this peak (present in *ca.* 5% yield) was identified tentatively as the allylic CH insertion product, 3-(1-chloro-2,2,2-trifluoroethyl)cyclohexene (I). Its infrared spectrum showed a band at 1646 cm^{-1} ($\nu_{C=C}$), and its ^1H nmr spectrum showed resonances in the vinyl hydrogen region. Nmr (in CCl_4, microcell, external standard) showed δ 1.48–2.68 (m, ring H), 3.18 (m, *ca.* 1 H, $CF_3CHClCH<$), 4.52 (m, *ca.* 1 H, CF_3CHCl-), and 5.58–6.47 ppm (m, *ca.* 2 H, vinyl H).

(b) Allyltrimethylsilane. The mercurial, 10.0 mmol, and 10 ml of the olefin were allowed to react in a sealed tube at 135° for 6 days. The usual work-up gave 2.57 g (72%) of phenylmercuric bromide and a trap-to-trap distillate which was distilled. A fraction distilling from 20 to 66° was examined by glc (column H, 45–80°) and found to contain benzene (19%) and trimethylchlorosilane (37%); samples of these were collected and identified by means of their glc retention times and nmr spectra. A high-boiling fraction, flashed over at 77° (40 mm), contained (glc, column E, 110°) the product, 1-chloro-1-trifluoromethyl-2-trimethylsilylmethylcyclopropane (mixed isomers, but not resolvable) in 9% yield. An analytical sample was isolated by glc (column H, 85°), $n^{25}D$ 1.4031.

Anal. Calcd for $C_8H_{14}ClF_3Si$: C, 41.64; H, 6.11. Found: C, 42.05; H, 6.20.

Mass spectrum (mixed isomers, 80 eV) *m/e* (relative intensity) (no M^+) 217, 215 (<1, 1:3 ratio, $[M - CH_3]^+$), 197, 195 (<1, 1:3 ratio, $[M - CH_3 - HF]^+$), 140, 138 (10, 31, $[M - Me_3SiF]^+$), 122 (8.7, $[M - Me_3SiCl]^+$), 103 (37, $[M - Me_3SiCl - F]^+$), 95, 93 (5.1, 15, Me_2ClSi^+), 77 (19, Me_2FSi^+), 73 (100, Me_3Si^+). Nmr (mixed isomers, $CHCl_3$, microcell) showed δ 0.01 (broad s, 9 H, Me_3Si), 0.60–1.00 (m, 3 H, cyclopropyl H), and 1.50 ppm (overlapping triplets, 2 H, Me_3SiCH_2).

(c) **Tetramethylethylene.** The mercurial, 20.0 mmol, and 74 mmol of the olefin in 10 ml of benzene were allowed to react in a sealed tube at 130° for 54 hr. The usual work-up gave phenylmercuric bromide in 83% yield, mp 277–279°, and a filtrate which was trap-to-trap distilled from 1.98 g of brown, tarry residue. The distillate contained (glc, column F, 90°) two products. The one with shorter glc retention time (58% yield, as determined later using column A at 100°) was identified as 1-chloro-2,2,3,3-tetramethyl-1-trifluoromethylcyclopropane, a volatile glass at room temperature.

Anal. Calcd for $C_8H_{12}ClF_3$: C, 47.89; H, 6.03; Cl, 17.67. Found: C, 48.21; H, 6.01; Cl, 17.88.

The nmr spectrum (in CCl_4) showed two overlapping singlets centered at 1.23 ppm.

The second product was identified tentatively as 2-chloro-1,1,1-trifluoro-3,4,4-trimethyl-2-pentene, (IV), and was present in 13% yield. An analytical sample was obtained using column H at 85°.

Anal. Calcd for $C_8H_{12}ClF_3$: C, 47.89; H, 6.03. Found: C, 47.92; H, 5.94.

Mass spectrum (80 eV) showed 202, 200 (1.3, 3.9, M^+), 187, 185 (3.7, 12.9, $[M - CH_3]^+$), 165 (100, $[M - Cl]^+$), 145 (17.9), 123 (13.6), 81 (20.2), 57 (38.0, $C_4H_9^+$), 55 (22.9), 43 (13.3), 39 (20.6). Nmr (neat in a microcell, external standard TMS) showed δ 1.42 (s, 9 H, $-CMe_3$) and 2.25 ppm (q, 3 H, J_{H-F} = 1.8 Hz, $C{=}CCH_3$); ir (in CCl_4) 3035 sh, 2970 s, 2910 sh, 2865 sh, 1591 m ($\nu_{C=C}$), 1476 m, 1459 sh, 1434 sh, 1402 w, 1379 s, 1370 sh, 1269 vs, 1242 sh, 1181 vs, 1141 vs, 1050 s, 1016 m, 931 s, 868 m, and 717 cm^{-1} m.

(d) **Trimethylethylene.** A 20-mmol sample of the mercury reagent and 63 mmol of the olefin in 15 ml of benzene were heated in a sealed tube for 182 hr at 135°. The usual work-up gave phenylmercuric bromide in 72% yield and a trap-to-trap distillate which was found by glc (column J, 80°) to contain one major product in 45% yield. A more polar analytical glc column (C at 80°) showed this product to be composed of two components in 3:1 ratio in order of increasing retention time. The major product was collected (column K, 50°) and shown to be the mixed isomers of 1-chloro-2,2,3-trimethyl-1-trifluoromethylcyclopropane, $n^{25}D$ 1.3881.

Anal. Calcd for $C_7H_{10}ClF_3$: C, 45.05; H, 5.40; Cl, 19.00. Found: C, 45.42; H, 5.48; Cl, 18.90.

The nmr spectrum ($CHCl_3$, microcell) showed δ 0.97–1.57 ppm and the ir spectrum showed cyclopropane hydrogen absorption at 3019 cm^{-1}.

(e) *cis*-**2-Butene.** A 20-mmol sample of the mercurial, 10 ml of the olefin, and 10 ml of chlorobenzene were heated at 135° in a sealed tube for 10 days. The usual work-up was followed by distillation of the trap-to-trap distillate using a Vigreux column to obtain a product concentrate at 100–130°. Preparative glc (column G, 50°) served to isolate three major products. Two of these were the isomers of *cis*-1-chloro-2,3-dimethyl-1-trifluoromethylcyclopropane. The less abundant isomer was detected as a slight shoulder on the trailing edge of the peak corresponding to the more abundant isomer, but estimation of the isomer ratio was not possible.

Anal. Calcd for $C_6H_8ClF_3$: C, 41.75; H, 4.67. Found: C, 41.91; H, 4.72.

The infrared spectrum showed the cyclopropyl hydrogen absorption at 3028 cm^{-1}. Glc analysis on column C, 46–130°, showed the cyclopropane yield to be 27%. No *trans*-1-chloro-2,3-dimethyl-1-trifluoromethylcyclopropane was detected. Glc examination of a synthetic mixture of the two cis isomers and the trans isomer under the same conditions demonstrated that these were resolvable, a small amount of the trans isomer appearing as a well-defined shoulder on the leading edge of the major cis isomer.

The third major product was identified as benzene (9% yield). The starting mercurial was recovered in 31% yield from the trap-to-trap distillation residue.

(f) *trans*-**2-Butene.** The same procedures as with the cis isomer were used in the reaction of 20.0 mmol of the mercury compound with 10 ml of the olefin in 10 ml of chlorobenzene at 135° for 10 days in a sealed tube. An identical work-up showed the presence of benzene (4%), 2-bromo-2-chloro-1,1,1-trifluoroethane (8%), and *trans*-1-chloro-2,3-dimethyl-1-trifluoromethylcyclopropane (2%) as the "major" products. The latter was characterized. Nmr (CCl_4, microcell) showed δ 0.97–1.44 (m, ring H) and 1.11 ppm (d superimposed on the m, J = 12 Hz, CH_3). The infrared spectrum showed cyclopropyl CH absorption at 3020 cm^{-1}.

A minor product with slightly longer retention time than the cyclopropane (column G, 50°) was identified tentatively as 2-chloro-1,1,1-trifluoro-3-methyl-2-pentene, $CF_3CCl{=}C(Me)C_2H_5$ (mixed isomers) by comparison of its spectra with those reported for $(CF_3)_2C{=}C(Me)CH_2CH_3$. Nmr (in CCl_4, microcell) showed δ 1.09 (t, J = 7.5 Hz, CH_2CH_3), 2.02 (q, J = 2.5 Hz, $=C{-}CH_3$), and 2.37 ppm (q, J = 7.5 Hz, CH_2CH_3). Each of the resonances showed fine structure, indicating that isomers may be present. Nmr reported for $(CF_3)_2C{=}C(Me)C_2H_5$ showed δ 1.19 (q, J = 7 Hz, CH_2CH_3), 2.11 (m, $=CCH_3$), and 2.46 ppm (q, J = 7 Hz, CH_2CH_3).[10] The infrared spectrum of (assumed) $CF_3CCl{=}C(Me)Et$ (in CCl_4) showed bands at 2978 w, 2940 w, 2880 w, 1787 w, 1636 w ($\nu_{C=C}$), 1457 w, 1374 w, 1349 w, 1300 s, 1250 m, 1215 m, 1169 vs, 1133 vs, 1103 m, 1071 w, 972 sh, 940 m, and 850 cm^{-1} w. The infrared spectrum of $(CF_3)_2C{=}C(Me)Et$[10] showed $\nu_{C=C}$ at 1647 cm^{-1}. A mixture of the cyclopropane and the olefin was analyzed.

Anal. Calcd for $C_6H_8ClF_3$: C, 41.75; H, 4.67. Found: C, 42.23; H, 4.85.

In this reaction the phenylmercuric bromide yield was 23% and starting mercurial recovery was 55%.

Reaction of $PhHgCClBrCF_3$ with Triethylsilane. The standard apparatus was charged with 20.0 mmol of the mercurial, 5.0 ml of triethylsilane (Peninsular ChemResearch), and 20 ml of chlorobenzene. The resulting clear solution was heated under nitrogen, with stirring, for 6 days at 126–130° (reflux), during which time a flaky white solid formed. Filtration under nitrogen of the reaction mixture afforded a trace of metallic mercury, 5.95 g (83%) of phenylmercuric bromide, and a clear yellow filtrate. The latter was trap-to-trap distilled, leaving 1.75 g of dark, oily residue. Glc examination of the distillate (column A, 130°) showed the presence of five products: benzene (1.6 mmol), triethylchlorosilane (5.1 mmol), triethylbromosilane (2.2 mmol), triethyl(1-chloro-2,2,2-trifluoroethyl)silane (52% yield), and triethyl(1-bromo-2,2,2-trifluoroethyl)silane (3%). The known compounds were identified by comparison of their glc retention times, ir spectra, and/or refractive indices with those of authentic samples. A 90% pure sample of $Et_3SiCHClCF_3$ was obtained by short-path distillation, bp 87–88° (35 mm). Further purification by preparative glc (column D, 148°) gave a pure sample, $n^{25}D$ 1.4150.

Anal. Calcd for $C_8H_{16}ClF_3Si$: C, 41.28; H, 6.93; Cl, 15.23. Found: C, 41.42; H, 6.98; Cl, 15.16.

Nmr (in CCl_4) showed δ 0.93 (m, 15 H, Et_3Si) and 3.53 ppm (q, J_{HF} = 10.4 Hz, 1 H, $CHClCF_3$); ir (liquid film) 2960 vs, 2919 sh, 2880 s, 1461 m, 1416 m, 1380 w, 1300 vs, 1258 vs, 1161 vs, 1136 vs, 1088 vs, 1008 s, 867 m, 819 m, 743 vs, and 668 cm^{-1} w.

A small sample of $Et_3SiCHBrCF_3$ could be isolated by glc from a higher boiling, 88–100° (35 mm), fraction. It became colored in a sealed capillary after 1 day in the dark and was only characterized spectroscopically: nmr (CCl_4, microcell) δ 0.93 (m, Et_3Si) and 3.47 ppm (q, J_{HF} = 10 Hz, $CHBrCF_3$); ir (liquid film) 2962 vs, 2920 sh, 2885 vs, 1459 m, 1414 m, 1380 w, 1288 vs, 1257 vs, 1145 vs, 1095 vs, 1080 vs, 1005 s, 866 m, 780 m, 729 s, 700 s, and 660 cm^{-1} w; mass spectrum (80 eV) *m/e* 249, 247 (0.4, 0.4, $[M - Et]^+$), 171, 169 (0.5, 0.5), 147, 145, (0.9, 0.9), 144, 142 (1.2, 1.2, $BrCH{=}CF_2^+$), 134 (24.1, Et_3SiF^+), 115 (18.2, Et_3Si^+), 105 (100, Et_2FSi^+), 87 (18.2, Et_2HSi^+), 77 (52.4, $EtHFSi^+$).

In another experiment carried out under identical conditions the yields of primary products were: PhHgBr, 63%; $Et_3SiCHClCF_3$, 51%; $Et_3SiCHBrCF_3$, 4%.

Reaction of $PhHgCClBrCF_3$ with Triphenylphosphine in the Presence of Benzaldehyde. Into the standard apparatus was charged 15.0 mmol of the mercury reagent, 3.94 g (15.0 mmol) of triphenylphosphine (M&T Chemicals, Inc.), 3.18 g (30.0 mmol) of redistilled benzaldehyde, and 25 ml of *p*-xylene. As the reaction mixture was heated slowly to reflux, a small amount of grey solid precipitated and the solution became dark. The reaction mixture was heated for 71 hr. The black mixture was filtered from a trace of mercury and 4.47 g of crude phenylmercuric bromide. Trap-to-trap distillation of the filtrate at 0.04 mm followed, leaving 4.88 g of black, tarry residue. The distillate was concentrated and short path distillation of the residue gave a fraction at 90–93° (46 mm). Preparative glc gave the expected Wittig reaction product as a cis–trans isomer mixture, $PhCH{=}CClCF_3$, $n^{25}D$ 1.4940. Glc analysis (column A, 120°) showed the product yield to be 38%. The isomer with longer retention time was slightly more abundant, the isomer ratio being 1.0:1.1. The mixture was analyzed.

Anal. Calcd for $C_9H_6ClF_3$: C, 52.32; H, 2.93; Cl, 17.16. Found: C, 52.72; H, 3.13; Cl, 16.70.

Nmr (mixture, neat sample in microcell, ^1H) showed δ 6.8–7.6 (m) (*ca.* 50% in PhCHO, ^{19}F, internal $PhCF_3$ standard, 63.747 ppm *vs.* $CFCl_3$), +5.66 (d, J_{HF} = 1.1 Hz, CF_3 cis to H) and −1.05 ppm (broad s, CF_3 trans to H). Samples of both isomers could be collected by glc using column F at 110–120°.

The residue from the trap-to-trap distillation of the filtrate was extracted with 150 ml of boiling cyclohexane. From the extracts triphenylphosphine oxide, mp 156–157°, could be isolated as white needles in 38% yield.

Reaction of Phenyl(1,1-dihalo-2,2,2-trifluoromethyl)mercury Compounds with Sodium Iodide in 1,2-Dimethoxyethane in the Presence of Cyclohexene. (a) **$PhHgCCl_2CF_3$.** The standard apparatus was charged with a solution containing 30.0 mmol of the mercury reagent, 10 ml of cyclohexene, and 50 ml of DME. The solution was heated to reflux and 4.82 g (32.2 mmol) of sodium iodide (powdered and dried for 24 hr at 110° and 0.05 mm) in 35 ml of DME was added slowly over 35 min. The reaction mixture became slightly yellow and cloudy during the addition; it was heated at reflux for an additional 4 hr and stirred at room temperature overnight. Filtration was followed by trap-to-trap distillation (0.1 mm, pot temperature to 35°, closed system) into a receiver at −78°. Glc analysis showed the presence of a single low-boiling product in addition to cyclohexene and solvent. In particular, 7-chloro-7-trifluoromethylnorcarane was not present. The product was isolated *via* distillation through a Widmer column (receiver cooled to −78°). The product obtained was identified as 1,1-dichloro-2,2-difluoroethylene by comparison of its gas phase infrared spectrum with that recorded in the literature: 1747 vs, 1326 vs, 1031 vs, and 991 cm^{-1} vs (bands broadened due to rotational structure) (lit.[35] 1749, 1327, 1032, 993 cm^{-1}). The yield of $CCl_2{=}CF_2$ (*via* glc, column A, 55°) was 60%.

(**b**) **$PhHgCClBrCF_3$.** Essentially the same procedure was used in the reaction of 14.0 mmol of the mercurial with 15.6 mmol of sodium iodide in 25 ml of DME in the presence of 5.0 ml of cyclohexene. Redistillation of the trap-to-trap distillate gave a fraction at 39–67° from which the product could be isolated by glc (column D, 75°). It was identified as 1-bromo-1-chloro-2,2-difluoroethylene by means of its infrared spectrum: (gas cell) 1730 vs, 1319 vs, 1021 vs, and 943 cm^{-1} vs (lit.[36] 1731, 1314, 1022, 945 cm^{-1}, major bands only). Glc (column I, 100°) established that $CClBr{=}CF_2$ had been formed in 68% yield. None of the 7-chloro-7-trifluoronorcarane was present.

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The Enolic $C_3H_6O\cdot^+$ Ion Formed from Aliphatic Ketones[1-3]

F. W. McLafferty,* D. J. McAdoo,[4] James S. Smith, and Richard Kornfeld

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received August 11, 1970*

Abstract: Contrary to previous postulations, the ubiquitous enolic $C_3H_6O\cdot^+$ ion found in ketone mass spectra decomposes mainly by rearrangement to an unstable acetone ion, **2** → **8**, not by simple cleavage loss of the methyl group, **2** → **7**. A methyl hydrogen can also rearrange through a four-membered ring intermediate to the methylene group, **2** → **11**, and both reactions exhibit substantial primary isotope effects. All six hydrogen atoms show nearly equivalent secondary isotope effects on the relative rates for the losses of the two methyl groups, consistent with their loss from the intermediate acetone ion. An unusual observation is that the two methyl groups are lost from this intermediate acetone ion at unequal rates; we suggest that this is due to incomplete randomization of energy before decomposition. Apparently this is the first case reported in which ion fragmentation is not independent of initial preparation. The fragmentations of isotopically labeled $C_3H_6O\cdot^+$ ions formed by the double hydrogen rearrangement of alkanones closely resemble the behavior of the enolic $C_3H_6O\cdot^+$ ions. This provides independent verification of the recent ion cyclotron resonance evidence of Djerassi and coworkers which shows that these double rearrangement ions have the enolic structure, in contrast to the oxonium ion structure postulated originally.

The odd-electron $C_3H_6O\cdot^+$ ion and its higher homologs are well known as characteristic peaks in the mass spectra of aliphatic ketones, arising from the rearrangement of a γ-hydrogen atom, **1** → **2**, or the sequential rearrangement of γ- and γ′-hydrogen atoms, **3** → **4** → **2** (Scheme I).[5-7] This ion is also the most abundant peak in the spectrum of 1-methylcyclobutanol (**5**).[8] Although these alkanone rearrangements have been among the most thoroughly studied of all electron-impact reactions,[5-10] there are many aspects of the unimolecular reactions of these enolic ions that are poorly understood. It was established only recently that the characteristic olefin loss from the enolic ion **4** proceeded mainly through rearrangement of hydrogen to the methylene group, **4** → **2**, not to the hydroxyl group, **4** → **6**.[2,9,10] Further, most reported reactions of such enolic ions are typical of reactions of the olefinic functionality, not of the hydroxyl group;[6,9] particular note has been made of the absence of any evidence for tautomerization of an enolic ion to the ketonic structure.[6,9,11]

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