$$T + CH_2F_2 \longrightarrow CHTF_2 + H$$
$$(CH_2ClF) \quad (CHTClF) \tag{1}$$
$$T + CHF_3 \longrightarrow CHTF_2 + F \tag{2}$$

In each case, the monofluorocarbene is then formed by the elimination of HF (or HCl)[4] from the excited dihalomethane molecule. The monofluorocarbenes so formed are radioactively labeled as CTF and are subsequently traced through the radioactivity of the products.

The relative yields of the labeled dihalomethane molecules surviving without decomposition and of the cyclopropyl fluoride molecules under a variety of conditions are summarized in Table I.

**Table I.** Formation of Cyclopropyl Fluoride by Monofluorocarbene Addition to Olefins

| Excited molecule | Gas pressure, cm — Parent | $C_2H_4$ | $O_2$ | Relative yield[a] |
|---|---|---|---|---|
| $CHTF_2$ | $CH_2F_2$, 54.0 | 22.9 | — | 45 ± 2[b] |
| $CHTF_2$ | $CH_2F_2$, 52.3 | 23.8 | 4.1 | 45 ± 2[b] |
| $CHTClF$ | $CH_2ClF$, 56.1 | 17.5 | 3.4 | 35 ± 2[b] |
| $CHTF_2$ | $CHF_3$, 45.4 | 21.5 | 3.7 | 100 ± 8[b] |
| $CHTF_2$ | $CHF_3$, 56.6 | 12.3 | 2.4 | 95 ± 8[b] |
| | | *trans*-$C_4H_8$-2 | | |
| $CHTF_2$ | $CH_2F_2$, 52.2 | 19.3 | 3.5 | 44 ± 1[c] |

[a] Excited molecule = 100. [b] Cyclopropyl fluoride-*t*. [c] Dimethylcyclopropyl fluoride-*t*.

Additional experiments have been performed with various other substrates as possible reactants for the monofluorocarbene. Reactions with simple gaseous olefins lead to the corresponding substituted cyclopropyl fluorides in stereospecific reactions, without any substantial preference for *syn* or *anti* isomers. The products expected from the insertion of CTF into ethylene or ethane were not observed.[5]

No prior reports of the reactions of monofluorocarbene are in the literature. The formation of CHF has been suggested as occurring in the mercury-sensitized photolysis of $CF_2{=}CHF$, as indicated by subsequent reactions with various olefinic substrates.[6] In these systems, the corresponding cyclic products have not been observed, and the postulated mechanism involves the elimination of HF from an excited cyclic intermediate with the formation of the corresponding allene. Experiments with deuterated substrates further indicated that such dehydrofluorination must involve the loss of H and F atoms originally attached to the same carbon atom. Since our own experiments result in stabilized cyclopropyl fluoride molecules at gas pressures comparable to those used in the mercury-sensitized photolysis of $CF_2{=}CHF$, the absence of the cyclic products in the latter experiments implies a different intermediate from that found in our experiments—perhaps a difference in the electronic state involved. Since the allenes formed by the subsequent 1,1-dehydrofluorination of cyclic compounds would always be unlabeled with radioactivity in our experiments, our failure to observe these radioactive products is without significance.

The higher percentage decomposition of $CHTF_2^*$ formed by replacement of F in $CHF_3$ than of H in $CH_2F_2$ presumably indicates a greater average excitation energy in the former case. Similar results have been observed in comparison of $CH_2TCl$ formed by T for $CH_3$ *vs.* T for H.[7]

Each system contained the halomethane parent molecule, ethylene, and $He^3$, and most also contained $O_2$. These irradiated systems are analyzed for their radioactive components by the usual techniques of radio gas chromatography,[2,8,9] utilizing a sufficient variety of separation columns to ensure isolation and identification of all of the radioactive components.

**Acknowledgment.** An authentic sample of cyclopropyl fluoride for calibration was kindly furnished to us by Professor A. F. Trotman-Dickenson. Dr. Hal Jackson kindly provided the samples of $CH_2F_2$ and $CH_2ClF$.

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(4) Excited CHTClF can decompose either by elimination of HCl to form CTF, or of HF to form CTCl. Both pathways are observed. Alternative decomposition paths also exist for each molecule in which the radioactive atom is eliminated as TF or TCl, leaving a halocarbene without radioactivity. No product is measured by the radio gas chromatographic technique in these cases.

(5) G. L. Closs and J. J. Coyle have shown [*J. Am. Chem. Soc.*, **84**, 4350 (1962); **87**, 4270 (1965)] that addition to the double bond is strongly favored *vs.* the formation of insertion products by CHCl, and that the latter reactions, when they do occur, show a strong preference for occurrence at the weaker C–H bonds.

(6) R. J. Norstrom, O. P. Strausz, and H. E. Gunning, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 4–9, 1965.

(7) Y.-N. Tang and F. S. Rowland, *J. Am. Chem. Soc.*, **87**, 3304 (1965).

(8) See, for example, "Chemical Effects of Nuclear Transformations," Vol. 2, International Atomic Energy Agency, Vienna, 1961.

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## Triphenylgermyl Hydroperoxide

*Sir:*

In a previous paper[1] the synthesis of silyl hydroperoxides has been described. We wish to report that the same preparative method has now yielded triphenylgermyl hydroperoxide. Although bisgermyl peroxides[2,3] and compounds containing a GeOOC structure[4] have been described, the corresponding hydroperoxides had not been investigated until the present work.

Triphenylbromogermane (2.0 g, 0.0052 mole) was dissolved in dry ether (200 ml), and 98% hydrogen peroxide (2 ml, 0.085 mole) was added. The mixture was stirred (2 min) and dry ammonia gas was bubbled through the solution for 30 sec. The reaction was then quenched by adding water (30 ml). The ether layer was separated, washed with water (two 10-ml portions), and then dried over magnesium sulfate. The ether was removed *in vacuo*, and the residue (1.25 g) was recrystallized twice from chloroform–hexane to give triphenylgermyl hydroperoxide (0.95 g, 54.5%), mp 135–136.5°. The compound does not decompose on melting, for if the molten mass is allowed to solidify, it remelts at 135–136.5°. The infrared spectrum of the hydroperoxide in carbon tetrachloride has a general qualitative similarity to the spectrum of triphenylsilyl

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(1) R. L. Dannley and G. Jalics, *J. Org. Chem.*, 30, 2417 (1965).

(2) A. G. Davies and C. D. Hall, *Chem. Ind.* (London), 1695 (1958).

(3) A. Rieche and J. Dahlmann, *Angew. Chem.*, 71, 194 (1959); *Ann.*, **675**, 19 (1964).

(4) A. G. Davies and C. D. Hall, *J. Chem. Soc.*, 3835 (1959).

hydroperoxide, including a strong peak at 2.8 $\mu$ characteristic of the OH group.

*Anal.* Calcd for $C_{18}H_{16}GeO_2$: C, 64.17; H, 4.79; Ge, 21.5; active O, 4.75. Found: C, 64.39; H, 4.84; Ge, 21.8; active O, 4.76. The molecular weight (vapor pressure osmometer) determined in benzene was 382, 383 (calcd for $C_{36}H_{16}GeO_2$: 336.9), indicating association of the hydroperoxide molecules in this solvent.

The hydroperoxide was also obtained from the reaction of 98% hydrogen peroxide with triphenylgermanium oxide (65% yield) and with triphenylgermanol (60% yield).

The hydroperoxide is quite stable and can be stored at −20° without any decomposition. When left at room temperature (*ca.* 25°) for 30 days, the active oxygen decreased only 2% (to 98%) and the melting point was unchanged.

Thermal decomposition of the hydroperoxide in *o*-dichlorobenzene at 160–170° gave the following products.

$$\underset{\text{1 mole}}{(C_6H_5)_3GeOOH} \longrightarrow \underset{0.65}{(C_6H_5)_3GeOH} + \underset{\textit{ca.}\ 0.20}{O_2} + \underset{\textit{ca.}\ 0.05}{[(C_6H_5)_2GeO]_x} + \underset{\textit{ca.}\ 20}{C_6H_5OH}$$

These products resemble those obtained from the thermal decompositions of triphenylsilyl hydroperoxide[5] and trimethyltin hydroperoxide.[6]

$$Ph_3SiOOH \longrightarrow \underset{0.45}{Ph_3SiOH} + \underset{0.23}{PhOH} + \underset{0.29}{Ph_2Si(OH)_2} + \text{polymer}$$

$$(CH_3)_3SnOOH \longrightarrow \underset{0.47}{(CH_3)_2SnO} + \underset{0.40}{CH_3OH} + \underset{0.49}{(CH_3)_2SnO} + \underset{0.24}{O_2}$$

The decomposition of the triphenylgermyl hydroperoxide has a first-order kinetic dependence on hydroperoxide concentration ($k = 2.38 \times 10^{-6}$ at 130°; $k = 4.34 \times 10^{-6}$ at 144°; $k = 13.3 \times 10^{-6}$ at 152°; $k = 22.0 \times 10^{-6}\ \text{sec}^{-1}$ at 163°). The energy of activation is 24.0 ± 1.0 kcal/mole. This is intermediate between the energies of activation for the first-order decompositions in nonpolar solvents of several silyl hydroperoxides (27 kcal/mole[5]) and that of trimethyltin hydroperoxide (21 kcal/mole[6]). Apparently an increased electropositive nature of the metal in these compounds leads to higher electron densities on the peroxide oxygens and thus promotes thermal dissociation.

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## Order of Electrophilic Substitution in 1,2-Dicarbaclovododecaborane(12) and Nuclear Magnetic Resonance Assignment

*Sir:*

Certain restrictions[1] relating the ground-state charge distributions to transition states may allow predictions of sequential order of electrophilic or nucleophilic substitution in carboranes[2] from molecular orbital theories.[2–4] Here we show that *o*-$B_{10}C_2H_{12}$ brominates[5] under Friedel–Crafts conditions, first at B-9 and B-12, and then at B-8 (B-10). Photochemical chlorination occurs last at B-3 and B-6. These results permit a unique $^{11}B$ nmr assignment and a test of molecular orbital predictions.

The positions of bromination are here firmly established from three-dimensional crystallographic studies of 9,12-dibromo-*o*-carborane ($Pbn2_1$; $a = 7.42$, $b = 13.03$, $c = 11.75$ A; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.07$ for 909 reflections), of 8,9,12-tribromo-*o*-carborane (C2/c, $a = 12.28$, $b = 8.54$, $c = 23.42$ A; $\beta = 90.3°$; $R = 0.12$ for 1132 reflections), and of C,C′-dimethyl-8,9,10,12-tetrabromo-*o*-carborane ($P2_1/n$; $a = 13.18$, $b = 14.49$, $c = 8.20$ A; $\beta = 96.3°$; $R = 0.11$ for 1370 reflections). The distinction of C from B in the ordered 9,12-$Br_2B_{10}H_8C_2H_2$ structure was achieved from results on bond distances, electron densities, atom multipliers, and thermal parameters.

Molecular orbital calculations, made by a new nonempirical method,[4,6] are based upon parameters obtained from self-consistent field molecular orbital calculations on $B_2H_6$ and $C_2H_6$ in which Slater exponents were used for B and C, and an exponent of 1.2 was employed for H. Framework charges on BH or CH units in *o*-$B_{10}C_2H_{12}$ are 0.29 for C-1, 0.26 for B-3, −0.02 for B-4, −0.28 for B-8, and −0.24 for B-9. If, however, those occupied molecular orbitals which lie highest in energy are more easily distorted by electrophilic reagents, we may note that the highest five MO's, which are within 0.02 atomic unit of one another and separated by 0.05 au from the next lowest orbital, place 0.79 electron on B-9 but only 0.60 electron on B-8. Perhaps this charge difference, which is reversed when a number of lower lying orbitals are added, may contribute to the preference of electrophilic reagents for B-9 over B-8.

Zakharkin and Kalinin[7] have noted that the number of isomers prepared from *o*-carborane, C-methyl-*o*-carborane, and C,C′-dimethyl-*o*-carborane suggests that halogen substitution occurs first at 9,12 and then at 8,10. They must assume that 3,6 substitution is excluded on the basis of the charge distribution as given by molecular orbital theory. Their second assumption, that substitution of $CH_3$ for H on C does not change the sequential ordering of substitution, is now partly, supported by our X-ray results on C,C′-dimethyl-8,9,10,12-tetrabromo-*o*-carborane, at least for tetrabromination.

The published[8–10] $^{11}B$ spectra of *o*- and *m*-carborane

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