charge product as is found in complexation reactions with an SN1 mechanism. Thus, the ratios of rate constants for different charge products are in reasonable agreement with those of the estimates[5,15,19,21] of the ion-pair association constant K_0. In particular, the ratio $k_4/k_2 = 7.7$ for the oxalate system is in good agreement with other experimental data[5,15,19,21] and a value for $K_0^{MOH^{2+},H_2X}/K_0^{MOH^{2+},HX^-}$ of about 10.[20,24]

Examination of the apparent enthalpies and entropies of the redox reactions in Table IV also lends some support to the assignment of an SN1 mechanism.[26] Enthalpies of activation increase as the enthalpy of ion-pair formation (eq 16) becomes more positive[18b] and the entropy of activation becomes increasingly positive as electrostriction of solvent in the transition state decreases.[23,25,26] The observed trends are in the direction expected from these considerations, the change being most marked in going from charge product 0 to charge product −2.

The large driving force[3,27] for reactions of cobalt(III) is evidently of primary importance[28] in determining the mechanism of its oxidation reactions in perchloric acid solution. It is also evident that the rates of decomposition of the mono(oxalato)cobalt(III) complexes are much greater than those of the higher oxalato complexes. Indeed, the rates of oxidation of oxalic acid by the weaker, labile oxidants cerium(IV),[29] chromium(VI),[30] and manganese(III)[31] would seem to be limited rather by the rates of decomposition of intermediate complexes than by the rates of their formation.

Acknowledgment.—The kinetic work described in this paper was carried out with help and advice from Dr. Norman Sutin at Brookhaven National Laboratory under the auspices of the United States Atomic Energy Commission, to whom we express our thanks. G. D. wishes also to thank I.C.I., Ltd., for financial support.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA 32601

A Series of 1,3-Dioxolanes Derived from Dilithium Perfluoropinacolate[1]

BY ALAN P. CONROY[2] AND R. D. DRESDNER*

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The ionic compound dilithium perfluoropinacolate, $Li_2[(CF_3)_2CO]_2$, can be prepared from lithium and perfluoroacetone in tetrahydrofuran. When this compound is allowed to react with a variety of labile dihalides such as $SOCl_2$, SO_2Cl_2, $COCl_2$, $C_6H_5BCl_2$, $C_6H_5PCl_2$, CrO_2Cl_2, $CF_3N{=}SF_2$, $CF_3CF_2N{=}SF_2$, or the tetrahalide of titanium, a series of 1,3-dioxolanes, $[(CF_3)_2CO]_2XY$, with the central atom of the halide in the 2 position, is produced. Thus X is S, C, B, P, Cr, or Ti and Y is O, O_2, C_6H_5, $=NR_f$, or Cl_2. The new substances prepared in this manner were identified by elemental and various spectral analyses.

Introduction

The chemistry of perfluoroacetone has been under serious investigation for several years and the more pertinent results have been well surveyed.[3] There exist also a vast number of examples of the preparation of a variety of 1,3-dioxolanes starting with a study by Fischer[4] and others,[5] who introduced atoms other than carbon into the 2 position of the five-membered ring. The known fluorine-containing analogous compounds have S, P, or Si atoms in the 2 position. These were obtained by the reactions of C_2F_4 and SO_3,[6] $(CF_3)_2CO$ and alkyl phosphines[7], and $(CF_3)_2CO$, Li, and $(CH_3)_2SiCl_2$,[8] respectively. The structure of the silicon-containing compound was reported initially as having the silicon atom in the 3 position. Subsequent studies[9] showed that the Si atom did in fact occupy the 2 position which was in accord with the structure of all other 1,3-dioxolanes reported.

The structures of 1,3-dioxolanes have been generally interpreted from nmr data. In at least one instance,[10] a half-chair configuration was assigned on the basis of

* To whom correspondence should be addressed.

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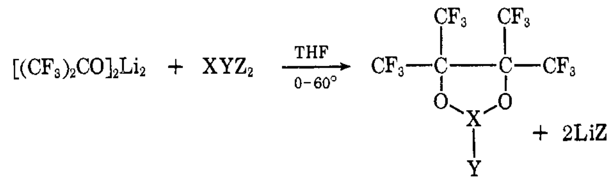
hydrolysis products. Evidence for nonplanar structures has also been obtained in temperature-dependent nmr studies. Two investigations of 2-methyl-1,3-dioxolane[11,12] manifested complex resonances which were attributed to ring flipping. However, temperature-dependent nmr studies of several 2-substituted 4,4,5,5-tetramethyl-1,3,2-dioxaphospholanes, in which the phosphorus atom was three-coordinate, were interpreted as resulting in no evidence that ring inversion occurred in the range investigated. Two resonances were observed, one each for the 4- and 5-methyl protons on different sides of the ring.[13] This same type of spectral behavior was observed in the case of 1,3,2-dioxothiolane.[14]

Discussion of Results

In the work reported in this paper, a series of new fluorocarbon dioxolanes was prepared and identified. Each new compound consisted of a five-membered ring system obtained from the reaction of dilithium perfluoropinacolate with a labile covalent dihalide or titanium tetrachloride. The general reaction can be described as



where X can be C, S, B, P, Ti, Cr; Y is an appropriate functional(s) group; and Z is Cl or F. The purified materials were stable to decomposition at room temperature for weeks. However, several tended to be susceptible to hydrolysis and were handled in a vacuum system or a drybox. The preparative reactions all proceeded spontaneously and most were observed to do so exothermally between 0 and 60°. Dilithium perfluoropinacolate (I), formed by the reaction of lithium with perfluoroacetone in tetrahydrofuran (THF), was impossible to free of solvent even on heating *in vacuo* up to 150°. The fact that the same reactions between I and various covalent halides—$COCl_2$, $SOCl_2$, SO_2Cl_2, $C_6H_5PCl_2$, $C_6H_5BCl_2$, $CF_3N{=}SF_2$, $C_2F_5N{=}SF_2$, CrO_2Cl_2, and $TiCl_4$—proceeded with almost equal spontaneity in four different solvents—THF, $(C_2H_5)_2O$, C_6H_6, and CCl_4—indicated that reactivity was not too dependent on solvent polarity.

THF was present in the products $[(CF_3)_2CO]_2CrO_2$ (X) and $[(CF_3)_2CO]_2TiCl_2$ (IX) even though the solvent used in their preparation was not THF. For example X, prepared in CCl_4, was also recrystallized from hot CCl_4 and was pumped on for 50 hr, yet its pmr spectrum in CCl_4 still showed more than trace amounts of THF to be present. A series of molecular weights on X determined in methanol using a vapor osmometer had an average value of 426 ± 4 (theory 416 for solvent-free X). The elemental analysis of X indicated that it was a 1:1 adduct. These data indicated that this adduct is 25% dissociated in methanol. Compound IX was also found to be a 1:1 adduct incorporating 1 mol of THF/mol of 1,3-titanolane. It has been observed[15] that in a reaction between $TiCl_4$ and ethylene glycol which resulted in the formation of a 1,3-titanolane, 2 mol of the glycol was solvated to the product molecule.

Attempts to prepare I in solvents other than THF, although moderately successful, resulted in yields so low that other solvents had to be abandoned.

The ir spectra of all the compounds had several common characteristics. These were in the 1100–1400-, 850–1100-, and 650–825-cm^{-1} regions which can be attributed to strong C–F, ring-breathing, and carbon skeletal vibrations, respectively. In the compounds $[(CF_3)_2CO]_2S{=}NCF_3$ (V) and $[(CF_3)_2CO]_2S{=}NC_2F_5$ (VI) the N=S assignments at 1380 and 1405 cm^{-1}, respectively, are strong and unequivocal. In the spectrum of compound IV, $[(CF_3)_2CO]_2C{=}O$, the C=O stretch vibration at 1915 cm^{-1} is more intense than any C—F band in the spectrum. Compound II, $[(CF_3)_2CO]_2S{=}O$, has a spectrum in which no S=O stretch assignment could be made. This is attributed to the fact that many S=O absorptions (1308 cm^{-1} in SOF_2 and 1383 cm^{-1} in SOF_4) are found in the C—F range and in this instance were masked. The spectrum of $[(CF_3)_2CO]_2SO_2$ (III) differs from that of II in only two minor observable ways. It has a strong peak at 1440 cm^{-1} and shoulder side bands on the C—F band at about 1195 cm^{-1} not prominent in the spectrum of II. The 1440-cm^{-1} value should be that for asymmetric stretching.

Correlation of the nmr spectra of these compounds focuses attention on a number of interesting structural relations. Compound I appears to have a pseudo-ring structure on the basis of both its ^{19}F nmr chemical shift (ϕ 70.5; singlet) and the "ring breathing" peaks in its ir spectrum.[16] The structures of compounds III, IV, $[(CF_3)_2CO]_2BC_6H_5$, V, IX, and X (singlets in ^{19}F nmr) have planar (on the nmr time scale) rings with the ligands on the heteroatom in the 2 position symmetrically disposed with respect to the plane and the CF_3 groups. On the other hand, in compounds II, $[(CF_3)_2CO]_2PC_6H_5$, VI, VII, and VIII, in which lone electron pairs are said to reside on the heteroatoms, the ligand in each case is repelled out of the ring plane causing the ^{19}F resonances of the methyl fluorine atoms to be in different magnetic environments, so that as a first approximation spin coupling occurs. A pattern observed in the spectra of compounds VII and VIII appears to be through space coupling of the N–CF_3 and

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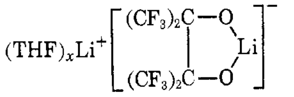


We are indebted to him for the suggestion.

N–CF_2– fluorine nuclei with those of the C–CF_3 fluorine nuclei in the 4 and 5 positions. Also in VIII there is no coupling observed between the N–CF_2 and N–CF_2–CF_3 neighboring F nuclei. Finally, as indicated above the ^{19}F nmr spectra of IX and X were singlets. While the singlet for IX was sharp, that for X was broad and the broadening is believed to be due to paramagnetic broadening from minute amounts of paramagnetic chromium impurities.

The molecular weights of those compounds which were liquid at around room temperature (II–VIII) were determined from mass spectra. The metal derivatives could not be volatilized without difficulty and parent peaks were not observed. However lower mass peaks from the spectra were sufficiently meaningful to confirm the identity of the several metal compounds.

No kinetic data have been obtained to verify a mechanism for the reactions. In general, however, the presence of perfluoropinacolate ions in polar solvents suggests a Lewis acid–base interaction with the elimination of halide ion from the acidic species. Each dihalide involved possessed Lewis acid character, by virtue of an available empty p or d orbital, except $COCl_2$. Shift of a pair of π electrons to the oxygen atom would empty a p orbital on this reagent.

An attempt to prepare $[(CF_3)_2CO]_2PF_3$ from PF_3Cl_2 failed to produce any quantity of material that was sufficiently stable to be isolated and identified.

Experimental Section

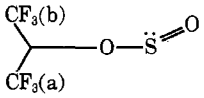
Most reactions were performed in an all-glass vacuum system. When necessary some vessels were loaded in a Vacuum Atmospheres Corp. Dry-Lab. Fractionations were carried out at atmospheric pressure in a 1.5 × 40 cm column packed with 4-mm single-turn glass helices. Vpc separations were accomplished in a 9 ft × 0.25 in. copper coil packed with dinonyl phthalate on Chromosorb P. The column was maintained at 100° and He was used as the transport gas.

Ir spectra were obtained on a Perkin-Elmer Model 237B double-beam grating spectrometer. Gases were handled in a 5-cm cell with NaCl optics, liquids were studied as neat films, and solids were dispersed in Nujol or KBr. The ^{19}F nmr spectra were obtained using a Varian DP-60 instrument at 56.4 MHz and an external standard. Pmr spectra were run using a Varian Model A-60 and TMS as an internal standard. Mass spectra were obtained with a Hitachi Perkin-Elmer RMV6E spectrometer applying an ionization voltage of 70 eV. A Perkin-Elmer Model 303B hollow cathode atomic absorbance spectrometer was used for the quantitative analyses of metals.

Materials.—Hexafluoroacetone (HFA) was obtained from Allied Chemical Corp. and was used as shipped. It had an ir spectrum that corresponded to that in the literature.[17] Lithium ribbon, $SOCl_2$, SO_2Cl_2, and $COCl_2$ were purchased from Matheson Coleman and Bell. The materials $TiCl_4$,[18] CrO_2Cl,[19] CF_3NSF_2, and $C_2F_5NSF_2$[20] were prepared according to the literature. Phenyl dichloroborane and $C_6H_5PCl_2$ were used directly as purchased from the Hynes Chemical Research Co. and K & K Laboratories, respectively. All solvents were reagent grade and were used freshly distilled from CaH_2 slurries.

Preparation of Compounds. Dilithium Perfluoropinacolate, $Li_2(CF_3)_2CO]_2$ (I).—To a 500-ml round-bottom flask were added 200 ml of dry THF and 1.4 g (0.20 g-atom) of Li ribbon in small pieces. The flask, which contained a magnetic stirring bar, was adapted to the vacuum system and slowly degassed. Then, 41.5 g (0.250 mol) of HFA was transferred from a reservoir to the reaction flask cooled to 0°. The HFA was absorbed slowly and in 1 hr the solution turned slowly from a pale yellow to a deep red-brown. The excess HFA and the THF were removed *in vacuo* and to the solid residue was added 150 ml of dried CCl_4. An apparently white precipitate formed. The mixture was filtered and the residue was washed three times with dry CCl_4 in the drybox. The filtrate containing the colored impurities was discarded. The white solid product weighed 21.2 g which corresponded to a yield of 61% based on the lithium. The ^{19}F nmr spectrum had a sharp singlet at a ϕ value of 70.5. The pmr spectrum in CH_3CN indicated that some THF was present in the system. The compound had a Λ_0 of 61.9 μmhos/cm in methanol at a concentration of 0.0521 *M*. Ir spectrum (cm^{-1}): 1300–1200 (s), (C–F), 1175 (sh), 1155 (sh), 1125 (m), 1055 (ms), 980 (w), 935 (ms), 885 (w), 870 (ms), 755 (w), 740 (ms), 735 (m), 720 (ms).

2-Oxo-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxathiolane, $[(CF_3)_2CO]_2SO$ (II).—Ten grams (0.0289 mol) of I was placed in a 250-ml three-neck flask adapted with a 125-ml funnel. To the flask were added 125 ml of dry THF and a mixture of 50 ml of THF and 3.60 g (0.0290 mol) of $SOCl_2$ which was added dropwise in a drybox. Heat was evolved. The mixture was stirred magnetically for 6 hr and then distilled. A major fraction was collected between 113 and 114°. This colorless liquid amounted to 6.0 g and was found to be very pure chromatographically. This is a yield of 55% based on the amount of I used. *Anal.* Calcd for $C_6F_{12}SO_3$: C, 18.95; F, 60.00; S, 8.42. Found: C, 18.23; F, 58.98; S, 7.72; mol wt (mass spectrometry) 380. Fluorine-19 mmr ϕ values: septets at (a) 67.8 and (b) 66.3 of equal area. Ir (cm^{-1}): 1300–1200 (s) (C—F) and (S=O), 1085 (ms), 1070 (s), 1010 (ms), 965 (s), 890 (s), 780 (s), 755 (s), 730 (w), 725 (s). The more pertinent mass peaks were CO^+ (100), CF_3^+ (100), S^+ (42), CF_3CO^+ (29), $C_5H_9SO_3^+$ (23), SO^+ (18), and $C_6F_{12}SO_3^+$ (11). This compound is assigned the conformation



II

2,2-Dioxo-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxathiolane, $[(CF_3)_2CO]_2SO_2$ (III).—Seventy-five milliliters of dry benzene and 9.83 g (0.0840 mol) of I were placed in a 125-ml erlenmeyer flask. To the slurry formed was added 3.83 g (0.0840 mol) of SO_2Cl_2 dropwise. The slurry tended to dissolve on vigorous magnetic stirring. After a few minutes, the solution turned brown and an apparently white solid began to precipitate. The reaction mixture was filtered 12 hr later. The precipitate was washed with dry benzene and freed of solvent. The precipitate was LiCl and amounted to 2.10 g. The residual solution was fractionated at 150 Torr, and a fraction, isolated between 38 and 35°, separated into two layers. The lighter layer was mainly benzene. The lower layer and the pot residue were combined, and the excess benzene was stripped off in the vacuum system. A solid residue which melted at 25° was sublimed from the system. It was colorless and amounted to 5.2 g, a yield of 40% based on I. This material had a micro boiling point of 131–132°. *Anal.* Calcd for $C_6F_{12}SO_4$: C, 18.18; F, 57.57; S, 8.08. Found: C, 18.51; F, 56.55; S, 7.97; mol wt (mass spectrometry) 396. Fluorine-19 nmr ϕ value: a sharp singlet at (a) 66.5. Ir (cm^{-1}): 1440 (s) (S=O), 1300–1200 (vs) (C—F), 1080 (sh), 1070 (sh), 970 (ms), 895 (ms), 805 (ms), 760 (ms), 720 (ms), 680 (w), 650 (m). The more pertinent mass spectrum assignments are CF_3^+ (100), $C_5F_9SO_3^+$ (24), CF_3CO (22), $C_6F_{11}SO_4^+$

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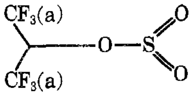
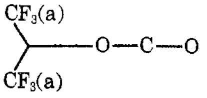
(16), $C_6F_{12}SO_4^+$ (14), and SO^+ (13). This compound is assigned the symmetric conformation



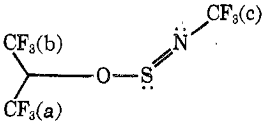
III

2-Oxo-4,4,5,5-tetrakis(trifluoromethyl)-1,3-dioxolane, $[(CF_3)_2CO]_2C{=}O$.—Ten grams (0.0289 mol) of I and 50 ml of dry THF were placed in a 250-ml round-bottom flask. The solution was degassed as it was stirred magnetically. Then, 2.97 g (0.0300 mol) of $COCl_2$ was expanded into the reaction vessel, cooled to 0°, from a reservoir. The mixture was stirred for 13 hr at 0°. When the mixture was allowed to warm to room temperature, two colorless liquid layers and some white solid residue were observed. The liquids were vacuum stripped from the flask leaving the solid. The less dense layer was mainly THF. The denser layer was purified by vpc. It was mainly THF and a pure substance amounting to 6.1 g which had a boiling point of 104.0–104.5°. The yield was not less than 58%. *Anal.* Calcd for $C_7F_{12}O_3$: C, 23.33; F, 63.33. Found: C, 23.23; F, 63.50; mol wt (mass spectrometry) 360. The ^{19}F nmr spectrum consisted of a sharp singlet with a ϕ value of (a) 68.4. Ir (cm^{-1}): 1925–1900 (vs) (C=O), 1835 (w), 1310–1170 (vs) (C—F), 1155 (vs), 1110–1080 (vs), 1010 (s), 960 (s), 925 (s), 890 (s), 765 (s), 755 (s), 735 (m), 725 (w), 700 (s). The more pertinent mass spectral peaks are CF_3^+ (100), CF_3CO (19), $C_4F_6O^+$ (14), $C_5F_9O^+$ (12), $C_6F_9O_3^+$ (6), and $C_7F_{12}O_3^+$ (2). This compound is assigned the conformation



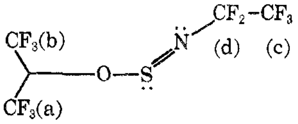
IV

2-Trifluoromethylimido-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxathiolane, $[(CF_3)_2CO]_2S{=}NCF_3$ (V).—Ten grams (0.0289 mol) of I was added to a 75-ml stainless steel cylinder adapted for vacuum line use. Twenty milliliters of THF was added to the evacuated vessel cooled to −190°. Then, 4.50 g (0.0289 mol) of $CF_3N{=}SF_2$ was condensed into the reactor which was sealed and heated at 60° for 20 hr. The reactor was allowed to cool to room temperature and was stripped of volatile materials which had a liquid volume of 26 ml. Fractionation of this clear liquid yielded 20 ml of THF and a 6.6-g fraction which had a normal boiling point of 99–101°. A small residue was discarded. This was a yield of not less than 51%. *Anal.* Calcd for $C_7F_{15}NSO_2$: C, 18.8; F, 63.7; N, 3.1; S, 7.2. Found: C, 18.1; F, 65.0; N, 2.5; S, 7.2; mol wt (mass spectrometry) 447. The ^{19}F nmr spectrum consisted of two broad multiplets each with a relative area of 2.0 and ϕ values of (a) 66.4 and (b) 66.0 and a septet with area of 1.0 and a ϕ value of (c) 47.7. Ir (cm^{-1}): 1380 (s) (N=S), 1300–1175 (vs) (C—F), 1065 (s), 1005 (m), 965 (ms), 890 (ms), 810 (m), 775 (m), 760 (ms), 740 (m), 725 (m), 710 (w). The pertinent mass spectral peaks are CF_3^+ (100), $C_6H_{12}NSO_2^+$ (36), CF_3CO^+ (28), CF_3NS^+ (21), SN^+ (18), $C_7H_{14}NSO_2$ (13), and $C_7F_{15}NSO_2$ (2). This compound is assigned the conformation



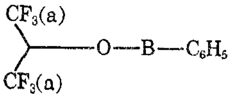
V

2-Perfluoroethylimido-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxathiolane, $[(CF_3)_2CO]_2S{=}NC_2F_5$ (VI).—To a 75-ml stainless steel reactor were added 10 g (0.029 mol) of I and 20 ml of THF. The cylinder was attached to a vacuum line and degassed at −190°. Then, 5.87 g (0.0289 mol) of $C_2F_5N{=}SF_2$ was condensed into the reactor, which warmed to 60° for 2 days. The vessel was allowed to cool to room temperature and was stripped *in vacuo* of its volatile contents which consisted of a light yellow liquid. The THF was stripped off the solution leaving a light yellow liquid residue which was purified by vpc. The purified product amounted to 7.47 g of a colorless liquid which boiled at 113.0–113.5°. The yield was 52%. *Anal.* Calcd for $C_8F_{17}NSO_2$: C, 19.3; F, 65.0; N, 2.80; S, 6.40. Found: C, 19.4; F, 65.2; N, 2.94; S, 6.23; mol wt (mass spectrometry) 497; however, the more prominent ion was $C_8F_{17}NSO_2^+$ of mass 478. The ^{19}F nmr spectrum consisted of four resonances at ϕ values of (a) 66.9, (b) 67.9, (c) 85.6, and (d) 86.1 with relative areas of 6, 6, 3, and 2, respectively. (a) was a broad multiplet, (b) a septet, (c) a sharp singlet, and (d) a well-resolved septet. It appears that both (d) and (b) were coupled to (a) whereas (c) was not coupled to any of the other nuclei. Ir (cm^{-1}): 1405 (s) (N=S), 1335–1200 (vs) (C—F), 1150 (s), 1135 (s), 1110 (s), 1085 (s), 1060 (s), 1030 (vs), 1000 (s), 965 (vs), 885 (s), 775 (s), 760 (vs), 740 (s), 725 (s), 715 (vs). The pertinent mass peaks are CF_3^+ (100), CF_3CO (30), $C_2F_5^+$ (12), SN^+ (12), $C_2F_4NS^+$ (12), $C_8F_{16}NSO_2^+$ (9), and $C_8F_{17}NSO_2^+$ (1). This substance is assigned the conformation



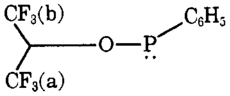
VI

2-Phenyl-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxaborolane, $[(CF_3)_2CO]BC_6H_5$ (VII).—Ten grams (0.0289 mol) of I and 50 ml of THF were mixed in a flask in the drybox. As the solution was stirred, 4.60 g (0.0289 mol) of $C_6H_5BCl_2$ was added to the solution dropwise. It became warm and cloudy. Three hours later the mixture was filtered. The white solid was LiCl. The filtrate was stripped of THF and a colorless liquid fraction boiling at 109.0–109.5° and amounting to 5.8 g was obtained. This represented a yield of 48%. *Anal.* Calcd for $C_{12}F_{12}H_5BO_2$: C, 34.3; F, 54.3; H, 1.20; B, 2.62. Found: C, 34.2; F, 54.0; H, 1.31; B, 2.98; mol wt (mass spectrometry) 447. The ^{19}F nmr spectrum was a sharp singlet with a ϕ value of 68.8. The pmr spectrum consisted of two characteristic C_6H_5 multiplets with τ values centered at 2.60 and 1.97. Ir (cm^{-1}): 1610 (ms), (C_6H_5), 1505 (w), 1440 (m), 1400 (s), 1365 (s), 1300–1200 (vs) (C–F), 1170 (s), 1110 (vs), 1070 (s), 1055 (m), 1035 (ms), 1010 (ms), 955 (s), 885 and 880 (ms), 825 (ms), 765 (ms), 745 (s), 735 (m), 715 (vs), 710 (w), 695 (ms), 610 (m). The more pertinent mass spectral fragments are C_5FHBO^+ (100), $C_{12}H_5F_{12}BO_2^+$ (82), CF_3^+ (73), $C_6H_5^+$ (35), CF_2^+ (14), CF_3CO (11), BO^+ (7), $C_{11}B_5F_{12}BO_2^+$ (5), CO^+ (4), and CF^+ (4). This substance is assigned the conformation



VII

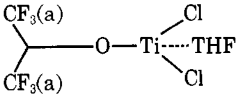
2-Phenyl-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxaphospholane, $[(CF_3)_2CO]_2PC_6H_5$ (VIII).—Fifty milliliters of dry benzene and 4.00 g (0.116 mol) of I were stirred vigorously in a 125-ml flask at 25° in the drybox. Then, 20.8 g (0.116 mol) of $C_6H_5PCl_2$ was added dropwise over a period of 0.5 hr. When approximately one-third of the $C_6H_5PCl_2$ had been added, a cloudiness appeared in the mixture and heat was evolved. Four hours later the solution was filtered. The solid residue was mostly LiCl and traces of I. It amounted to 11.1 g. The filtrate was stripped of benzene. A very pure distillation fraction amounting to 33 g was obtained at 204–205°. This was a yield of not less than 72%. *Anal.* Calcd for $C_{12}F_{12}H_5PO_2$: C, 32.7; F, 51.8; H, 1.16; P, 7.47. Found: C, 33.0; F, 52.1; H, 1.28; P, 7.47; mol wt (mass spectrometry) 440. The ^{19}F nmr spectrum appeared as two broad multiplets (more than seven peaks) of equal area centered at ϕ values of (a) 65.4 and (b) 66.8. Coupling with phosphorus was apparent. The pmr spectrum had τ values centered at 2.65 and 2.24. Ir (cm^{-1}): 1590–1440 (w–m) (C_6H_5), 1300–1200 (vs), (C–F), 1160 (sh), 1100 (s), 1075 (vs), 1035 (w), 1005 (ms), 975 (sh), 950 (vs), 885 (s), 810 (s), 775 (ms), 755 (s), 715 (vs), 710 (w, sh), 695 (ms). The pertinent mass spectral peaks are $C_4F_5^+$ (>100), $C_6H_5^+$ (100), CF_2^+ (70), $C_6H_4P^+$ (61), CF_3^+ (69), $C_6H_5PF^+$ (57), $C_{12}F_{11}H_5PO_2^+$ (55), $C_6H_5P^+$ (28), PO^+ (15), $C_{11}F_9PO_2^+$ (6), $C_{12}F_{12}H_2PO_2^+$ (3), and $C_{12}F_{12}H_5PO_2^+$ (1). This substance was assigned the conformation



VIII

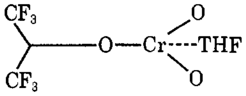
2,2-Dichloro-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxatitanolane Tetrahydrofuranate, $[(CF_3)_2CO]_2TiCl_2 \cdot THF$ (IX).—Thirty grams (0.0867 mol) of I and 50 ml of dried CCl_4 were placed in a 125-ml flask in the drybox. A slurry formed which was magnetically stirred with vigor as 16.4 g (0.0867 mol) of $TiCl_4$ was added dropwise over a 15-min period. Then all solids had dissolved. Five minutes later a white precipitate formed with the evolution of heat. Two hours later the mixture was filtered yielding 6.5 g of LiCl solid and a light yellow filtrate which was stripped of CCl_4 leaving a pale yellow crystalline solid. The yellow solid was recrystallized from hot CCl_4 and was recovered as almost colorless needle-shaped crystals which melted between 70.5 and 72.5°. They amounted to 28.2 g or a yield of not less than 72%. *Anal.* Calcd for $C_{10}F_{12}TiO_3Cl_2H_8$: C, 16.60; H, 1.53; F, 43.59; Ti, 9.18. Found: C, 17.16; H, 1.40; F, 41.94; Ti, 9.14. The ^{19}F nmr spectrum was a sharp singlet at a ϕ value of 67.6. The pmr spectrum of a sample dissolved in CCl_4 was two multiplets whose τ values were not shifted on addition of several drops of pure THF. Ir (cm^{-1}) in KBr: 1540 (w), 1500–1190 (s, br), 1150 (m), 1110 (s), 1035 (w), 895 (ms), 955 (w), 930 (ms), 880 (ms), 830 (ms), 770 (s), 750 (s), 730 (ms), 720 (s), 705 (s).

The heaviest positive ion observed in the mass spectrum was 345 (mol wt 523 with THF, 451 unsolvated). Excluding most Cl and Ti isotopic effects the pertinent fragments are CF_3^+ (100), $C_4H_8O^+$ (85), $C_4H_7O^+$ (79), CF_3CO^+ (60), $TiCl_2^+$ (30), $TiCl^+$ (16), Ti^+ (12 + 12), CF_2^+ (12), Cl^+ (12), CO^+ (9), and $C_6F_{11}TiO^+$ (7). This substance is assigned the conformation shown above.



IX

2,2-Dioxo-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxachromatolene Tetrahydrofuranate, $[(CF_3)_2CO]_2CrO_2 \cdot THF$ (X).—Twenty grams (0.0578 mol) of I was stirred in 100 ml of dried CCl_4 in a 250-ml flask in a drybox. Nine grams (0.0578 mol) of CrO_2Cl_2 dissolved in 15 ml of dried CCl_4 was added to the slurry dropwise over a 20-min period. The slurry dissolved and shortly thereafter an apparent white precipitate formed with the evolution of heat. As the mixture was stirred for 2 hr, it slowly turned dark green and more "white" solid formed. The mixture was vacuum stripped of CCl_4. The very dark, almost black, solid residue was extracted for 20 hr in a Soxhlet extractor with dry CCl_4. The residue was an off-white solid, mainly LiCl, and amounted to 3.4 g. The extract was very dark blue. The solvent was stripped away leaving a blue-black solid amounting to 22.8 g. This was recrystallized from boiling CCl_4 and dried *in vacuo*. This purified residue amounting to 17.4 g, a yield of at least 74%, melted between 152.0 and 152.5°. *Anal.* Calcd for $C_{10}F_{12}H_8CrO_5$: C, 24.59; H, 1.64, F, 46.72; Cr, 9.83. Found: C, 25.07; H, 1.65; F, 46.28; Cr, 9.58. The pmr spectrum was exactly the same as that observed for IX. The ^{19}F nmr spectrum consisted of a single paramagnetically broadened peak centered at a ϕ value of 62.7. Ir (cm^{-1}) (KBr pellet): broad weak peak centered at 1625, 1300–1175 (s) (C–F), 1070 (s), 1035 (w), 1020 (w), 980 (w), 940 (ms), 870 (ms), 760 (m), 750 (m), 735 (m), 715 (m), 700 (m). No fragment heavier than 223 (mol wt 488 or 416) was observed in the mass spectrum. The more prominent peaks are CF_3^+ (100), $C_4H_8O^+$ (90), $C_4H_7O^+$ (82), CO^+ (54), CF_3CO^+ (39), CF^+ (29), CF_3COCr^+ (25), CF_2^+ (12), $C_2F_3CrO_4^+$ (2), and $C_5F_5CrO^+$ (2). This substance is assigned the conformation



X

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138

Approximate Wave Functions for Carboranes Parametrized from Self-Consistent Field Model Calculations

BY THOMAS F. KOETZLE[1] AND WILLIAM N. LIPSCOMB*

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Molecular orbitals have been obtained by a nonempirical method for carboranes in the series $B_nC_2H_{n+2}$, using parameters from minimum basis set SCF calculations for $B_4C_2H_6$. Molecular energies, ionization potentials, charge distributions, and dipole moments have been calculated, and certain predictions made concerning *relative* reactivities of B atoms within each of these molecules.

In the past, the carboranes have been the subject of many theoretical studies utilizing molecular orbitals (MO) expressed as a linear combination of atomic orbitals (LCAO). Approximate wave functions have been calculated by both the extended Hückel method[2] and the nonempirical molecular orbital (NEMO)

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* To whom correspondence shoud be addressed.

[1] NIH Predoctoral Fellow, 1967–1969.

[2] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3489 (1962).