(+)$_{546}$-β-[Co(trien)(OH$_2$)$_2$]$^{+3}$ → (+)$_{546}$-β-[Co(trien)(NO$_2$)$_2$]$^{+}$. (a).—Optically pure (+)$_{546}$-β-[Co(trien)(OH$_2$)$_2$](ClO$_4$)$_3$ (3.78×10^{-3} *M*) in HClO$_4$ (0.01 *N*) was treated with excess NaNO$_2$. The orange diaquo complex changed to the yellow dinitro compound in about 10 min. and the following rotations were measured subsequently: 0.25 hr. [M]$_{546}$ +1540°, 0.5 hr. [M]$_{546}$ +1480°, 15 hr. [M]$_{546}$ +1060°. The rotation at 15 hr. corresponded to that for the fully resolved (+)$_{546}$-β-[Co(trien)(NO$_2$)$_2$-ClO$_4$, [M]$_{546}$ +1120°. The change in rotation was attributed to nitrito–nitro isomerization.

(b).—(+)-β-[Co(trien)CO$_3$]ClO$_4$·H$_2$O, [M]$_D$ +2890° (0.38 g.) was dissolved in water (5 ml.) and HClO$_4$ (2.1 ml. of 1 *N*) was added. After 20 min. excess NaNO$_2$ (0.4 g.) was added to form the dinitro complex which began to crystallize from the orange solution (pH 4) (10 min.), and the product was filtered off after 1.5 days. The orange filtrate was acidified with 1 drop of glacial acetic acid and NaClO$_4$ (0.07 g.) was added. Evaporation of this solution to 3 ml. gave a further yield of dinitro product. The combined fractions were washed with methanol and acetone and dried in air; total yield 0.36 g. (91%). A 0.195% solution gave α_{546} +0.53° when [M]$_{546}$ was +1080° and the visible absorption spectrum corresponded to that of the pure β-dinitro isomer. *Anal.* Calcd. for [CoC$_6$H$_{18}$N$_4$(NO)$_2$]ClO$_4$: C, 18.2; H, 4.6; N, 21.2. Found: C, 18.3; H, 4.7; N, 21.3. The RD curves for the solution and isolated sample were identical, Figure 16.

(+)-α-[Co(trien)Cl$_2$]$^{+}$ → (+)-α-[Co(trien)ClOH$_2$]$^{+2}$.—The half-life of aquation of α-[Co(trien)Cl$_2$]ClO$_4$, [α]$_D$ +2330°, was 80 min. at 25° in HClO$_4$ (0.01 *N*) so that its RD curve was measured quickly at 20° in 2.0×10^{-3} *M* solution and is given in Figure 7. The α-dichloro solution above was allowed to stand for 10 hr. at 20°. At this stage the maximum amount (97%) of chloroaquo ion was present and the rotations remained constant for 40 hr. The RD curve of this solution was measured since the chloroaquo salt could not be isolated, and the result is given in Figure 8.

(+)-α-[Co(trien)ClOH$_2$]$^{+}$ → (+)-α-[Co(trien)CO$_3$]$^{+}$.—This transformation was carried out as described for the β isomer. (+)-α-[Co(trien)Cl$_2$]ClO$_4$ aquated for 16 and 43 hr. gave the same rotation for the carbonato salt after treatment with NaHCO$_3$, [M]$_D$ +4700°, and no further change in rotation occurred in 24 hr. at 20°. The RD curve is given in Figure 9.

(+)-α-[Co(trien)Cl$_2$]ClO$_4$, [α]$_D$ +2330° (0.1 g.), was dissolved in HClO$_4$ (0.01 *M*) and after 15 hr. at 20° NaHCO$_3$ (0.06 g.) and NaClO$_4$ (0.05 g.) were added. The red solution, evaporated at 20°, gave a total yield of carbonatoperchlorate of 0.093 g. (92%) which was washed with methanol and acetone and dried in air. A 0.0792% aqueous solution gave α_D +0.96°, α_{578} +1.18°, α_{546} +1.25°, when [M]$_D$ +4630°, [M]$_{578}$ +5700°, [M]$_{546}$ +6030°. *Anal.* Calcd. for [Co(C$_6$H$_{18}$N$_4$)CO$_3$]ClO$_4$·H$_2$O: C, 22.0; H, 5.3; N, 14.6. Found: C, 21.8; H, 5.3; N, 14.7. Fractional recrystallization of the carbonato complex from water gave maximum rotations of [M]$_D$ +4730°, [M]$_{578}$ +5920°, and [M]$_{546}$ +6170°.

The carbonato complex was also isolated as the tetraphenylborate (+)-α-[Co(trien)CO$_3$][B(C$_6$H$_5$)$_4$]·2H$_2$O, [M]$_D$ +4730°. It was insoluble in water but dissolved in aqueous acetone. *Anal.* Calcd. for [Co(C$_6$H$_{18}$N$_4$)CO$_3$][B(C$_6$H$_5$)$_4$]·2H$_2$O: C, 60.1; H, 6.8; N, 9.0. Found: C, 60.8; H, 6.7; N, 8.9.

(+)-α-[Co(trien)CO$_3$]$^{+}$ → (+)$_{546}$-α-[Co(trien)(OH$_2$)$_2$]$^{+3}$.—(+)-α-[Co(trien)CO$_3$]ClO$_4$·H$_2$O, [M]$_D$ +4630° (2.0×10^{-3} *M* aqueous solution from the transformation above), was converted to the α-diaquo complex with HClO$_4$ as described for the β isomer. The carmine solution gave the rotations [M]$_D$ −950° (α_D −0.19°), [M]$_{578}$ −300°, [M]$_{546}$ +4700°, and the RD curve is given in Figure 10.

The isolated (+)-α-[Co(trien)CO$_3$]ClO$_4$·H$_2$O, [α]$_D$ +1200° (10 ml. of 2.14×10^{-3} *M* solution) was also converted to the diaquo ion with 1 drop of concentrated HClO$_4$ and the following rotations were measured after 20 min., [M]$_D$ −930° (α_D −0.20°), [M]$_{578}$ −190°, [M]$_{546}$ +4750°. The diaquo complex was also isolated from more concentrated solutions containing excess perchloric acid.

(+)$_{546}$-α-[Co(trien)(OH$_2$)$_2$]$^{+3}$ → (+)$_{546}$-α-[Co(trien)(NO$_2$)$_2$]$^{+}$.—(+)-α-[Co(trien)Cl$_2$]ClO$_4$, [α]$_D$ +2250° (1.00 g. in HClO$_4$, 50 ml. of 1.2×10^{-3} *M*), was aquated for 12 hr. at 20° and excess NaHCO$_3$ (0.46 g.) was added followed by excess HClO$_4$ (7.8 ml. of 1.0 *M*) after a further 30 min. The resulting diaquo solution was then treated (50 min.) with excess NaNO$_2$ (1.8 g.). The (+)$_{546}$-α-[Co(trien)(NO$_2$)$_2$]ClO$_4$ slowly crystallized and three fractions were obtained which were washed with NaClO$_4$ solution, alcohol, and ether and dried. Each fraction had the same rotation, [M]$_{546}$ +220° (α_{546} +0.11° for 0.2% aqueous solution), [M]$_D$ −20° (±20°), [M]$_{578}$ +20° (±20°); yield 0.95 g., 90%. The RD curve is given in Figure 11. *Anal.* Calcd. for [Co(C$_6$H$_{18}$N$_4$)(NO$_2$)$_2$]ClO$_4$: C, 18.2; H, 4.6; N, 21.2. Found: C, 18.1; H, 4.6; N, 20.5.

This transformation was repeated using (+)-α-[Co(trien)Cl$_2$]ClO$_4$, [α]$_D$ +2300° (0.100 g.). The dinitro product was not isolated but the final volume was adjusted to 50 ml. and the rotation, measured after 2 days, was α_{546} +0.11°, [M]$_{456}$ +210°. The RD curve was also similar to that of the isolated sample. The formation of the yellow α-dinitro complex was considerably slower than for the β isomer.

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Reactions of Hexafluorocyclobutanone with Metalloid Compounds

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Hexafluorocyclobutanone, a highly polarized ketone, reacts with boron halides to give esters of 1-halohexafluorocyclobutanol. Similarly, silanes add to the ketone to give hexafluorocyclobutoxy derivatives. Phosphines add in the opposite direction to give 1-hydroxyhexafluorocyclobutylphosphines.

Hexafluorocyclobutanone (1) is one of the most reactive ketones ever reported.[1] The exceptional reactivity may be attributed to a combination of ring strain and the electron-withdrawing influence of the fluorine atoms. Both forces tend to reinforce the normal

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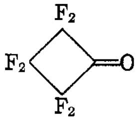
(1) D. C. England, *J. Am. Chem. Soc.*, **83**, 2205 (1961).

polarization of the ketone, $>C^{+}-O^{-}$, and to stabilize addition products such as heptafluorocyclobutanol, which is formed by addition of HF to the ketone.[2] As discussed in detail below, a number of metalloid compounds react with hexafluorocyclobutanone to give products which may be predicted on the basis of addition to the polar resonance form.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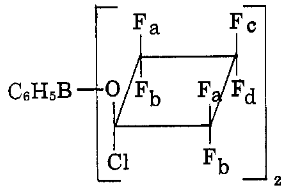
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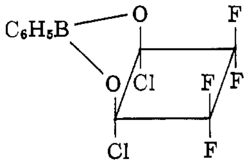
Boron Halides.—Phenyldichloroborane reacts with hexafluorocyclobutanone at room temperature to give the di-1-chlorohexafluorocyclobutyl ester (2). Similarly BCl_3 gives $B[OCCl(CF_2)_3]_3$. Both esters are colorless, organic-soluble liquids which rapidly hydrolyze in water or in moist air. The initial hydrolysis products appear to be the ketone hydrates and boric acid.

The fluorine n.m.r. spectra of these esters consist of two sets of AB patterns. The smaller set (relative intensity 1) arises from mutual coupling of fluorines c and d. These two fluorine atoms on carbon 3 are rendered nonequivalent by the presence of unlike substituents on carbon 1. Similarly, the "up" fluorines on carbons 2 and 4 differ from the "down" fluorines and give a similar pattern of relative intensity 2. The coupling (J = 210–230 c.p.s.) between the two fluorines on each carbon is comparable to that previously observed for unsymmetrical cyclobutanes.[3]

Tetrafluoro-1,2-cyclobutanedione[1] reacts with phenyldichloroborane to give the cyclic ester **3**. This cyclobutylene ester, in contrast to the simple ester **2**, is a solid, but, like **2**, hydrolyzes readily in moist air.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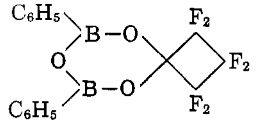
The F^{19} n.m.r. spectrum consists of a single AB pattern (J = *ca.* 225 c.p.s.) due to the dissymmetry of the fluorine atoms on carbons 3 and 4.

An attempt to prepare a phenylboronate ester of heptafluorocyclobutanol gave an unusual ketal anhydride (**4**). A mixture of BF_3, phenylboronic anhydride, and hexafluorocyclobutanone was allowed to react to prepare $C_6H_5BF_2$ and, simultaneously, to add its B–F functions to the fluoroketone carbonyl group. Instead, cycloaddition of the anhydride to the carbonyl seems to have occurred. The F^{19} n.m.r. spectrum of the crystalline product shows two peaks (2:1 intensity ratio), as would be predicted for a symmetrical 1,1-disubstituted hexafluorocyclobutane ring.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$(n\text{-}C_3H_7)_2Si[OCH(CF_2)_3]_2$

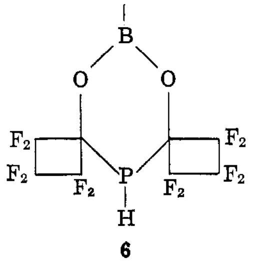
5

Dipropylsilane.—The reaction of a silane with hexafluorocyclobutanone was attempted in order to establish the direction of addition of the Si–H bond to the carbonyl function. The formation of bis(hexafluorocyclobutoxy)silane (**5**) indicates that the Si–H bond reacted as a hydride rather than an acid. The direction of addition was established by the presence of Si–O and the absence of O–H stretching bands in the infrared spectrum. In addition, the product was unreactive to acetyl chloride and phenyldichloroborane, although it did hydrolyze readily in water.

Phosphine.—Hexafluorocyclobutanone reacts with PH_3 at room temperature to give $(CF_2)_3C{<}^{OH}_{PH_2}$ and $[(CF_2)_3C(OH)]_2PH$. The direction of addition is consistent with addition of the relatively acidic PH to the polar form of the ketone. The relative ratio of the two phosphines formed in the reaction is determined by the ratio of reactants. An excess of PH_3 gives mostly the primary phosphine while an excess of ketone gives the crystalline secondary phosphine in almost quantitative yield.

The fluorine n.m.r. spectra of both phosphines show two sets of AB patterns (2:1 ratio) with coupling constants similar to those found for the boron esters. The proton resonance spectrum of $(CF_2)_3C{<}^{OH}_{PH_2}$ contains PH and OH absorption in a 2:1 ratio. Strong P–H coupling (J_{PH} = 202 c.p.s.) occurs in addition to weak coupling (J_{FH} = 1–5 c.p.s.) of the PH_2 protons with all the fluorine nuclei.

Both phosphines are stable to hydrolysis but are oxidized by air to give oily products. The secondary phosphine and diethyl phenylboronate undergo ester exchange to give the unusual heterocyclic ester **6** in high yield.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Experimental

Tris(1-chlorohexafluorocyclobutyl) Borate.—A Carius tube containing 0.90 g. of boron trichloride and 4.1 g. of hexafluorocyclobutanone was allowed to stand at room temperature for 3 days. Distillation of the crude liquid product gave 1.2 ml. of tris(1-chlorohexafluorocyclobutyl) borate[4]; b.p. 87–88° (5 mm.);

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[2] S. Andreades and D. C. England, *J. Am. Chem. Soc.*, **83**, 4670 (1961).

[3] W. D. Phillips, *J. Chem. Phys.*, **25**, 949 (1956).

[4] E. L. Muetterties and G. W. Parshall, U. S. Patent 3,052,710 (1962).

n^{25}D 1.344. The ester was miscible with benzene, ether, and acetone but hydrolyzed instantly in water to give boric acid.

Anal. Calcd. for $C_{12}BCl_3F_{18}O_3$: B, 1.66; F, 52.5. Found: B, 2.03; F, 52.6.

The infrared spectrum showed B–O stretching absorption at 1360 cm.$^{-1}$ in addition to strong C–F and C–Cl bands. The F^{19} spectrum was very similar to that described in detail below for the phenylboronate ester.

Bis(1-chlorohexafluorocyclobutyl) Phenylboronate.—The reaction of 1.6 g. of phenyldichloroborane with 4.5 g. of hexafluorocyclobutanone at 25° for 16 hr. gave a clear, colorless liquid. Two successive distillations gave 1.6 ml. of bis(1-chlorohexafluorocyclobutyl) phenylboronate (**2**); b.p. 52° (0.05 mm.); n^{25}D 1.4117.

Anal. Calcd. for $C_{14}H_5BCl_2F_{12}O_2$: C, 32.6; H, 0.98; B, 2.10; F, 44.3. Found: C, 32.0; H, 1.07; B, 2.18; F, 44.4.

The infrared spectrum showed aromatic C—H and C=C bands at 3070 and 1611 cm.$^{-1}$, B—O stretching at 1360 cm.$^{-1}$, and strong C—F and C—O absorption in the 1250 cm.$^{-1}$ region. The proton magnetic resonance spectrum (60 Mc./sec.) showed aromatic absorption of relative intensity 2 at -7.56 p.p.m. and another of intensity 3 at -7.00 p.p.m. relative to tetramethylsilane as an internal reference. The F^{19} n.m.r. spectrum showed an AB pattern of intensity 2 (Δ_{AB} = 5.9 p.p.m., J_{AB} = 210 c.p.s.) centered at 59.3 p.p.m. to high field from 1,2-difluorotetrachloroethane (external reference). An AB pattern of intensity 1 (Δ_{AB} = 5.6 p.p.m., J_{AB} = 230 c.p.s.) was centered at +63.4 p.p.m. The F^{19} spectra were recorded at both 40 and 56.4 Mc./sec. with the sample as a neat liquid.

1,2-Cyclobutylene Ester.—A mixture of 23 g. of phenyldichloroborane, 19 g. of tetrafluoro-1,2-cyclobutanedione, and 50 ml. of dichloromethane was allowed to stand at room temperature for 16 hr. The blue color of the diketone gradually disappeared, and the liquid phase became tan. The dichloromethane and excess phenyldichloroborane were distilled under reduced pressure. The residue was sublimed at 50° (0.1 mm.) to give 10 g. of white, crystalline 3-phenyl-1,5-dichloro-6,6,7,7-tetrafluoro-3-bora-2,4-dioxabicyclo[3.2.0]heptane (**3**), m.p. 55°.

Anal. Calcd. for $C_{10}H_5BCl_2F_4O_2$: C, 38.1; H, 1.60; B, 3.44; F, 24.1 Found: C, 38.3; H, 1.74; B, 3.53; F, 23.6.

The infrared spectrum showed aromatic C=C bands at 1503 and 1610 cm.$^{-1}$, B—O stretching at 1350 cm.$^{-1}$, and strong C—F bands in the 1000–1250 cm.$^{-1}$ region.

Reaction of Hexafluorocyclobutanone with Phenylboronic Anhydride.—A Carius tube containing 15.6 g. of phenylboronic anhydride, 6.1 g. of boron trifluoride, and 17.8 g. of hexafluorocyclobutanone was allowed to stand at room temperature for 2 days. The moist white solid which formed sublimed at 160–165° (8 mm.) to give 6.7 g. of white crystals of **4**, m.p. 78–82°.

Anal. Calcd. for $C_{16}H_{10}B_2F_6O_3$: B, 5.61; F, 29.5. Found: B, 5.18; F, 30.7.

The infrared spectrum showed aromatic C=C bands at 1500 and 1613 cm.$^{-1}$, very strong B—O stretching at 1355 cm.$^{-1}$, and C—F absorption at 1200 and 1310 cm.$^{-1}$.

Dipropylbis(hexafluorocyclobutoxy)silane.—A mixture of 2.3 g. of di-*n*-propylsilane and 8.9 g. of hexafluorocyclobutanone was heated at 100° for 16 hr. in a sealed glass tube. Distillation of the liquid product gave 4.5 g. (48%) of di-*n*-propyldihexafluorocyclobutoxysilane (**5**); b.p. 108–110° (25 mm.); n^{25}D 1.3558.

Anal. Calcd. for $C_{14}H_{16}F_{12}O_2Si$: F, 48.3; Si, 5.94. Found: F, 47.7; Si, 5.62.

The infrared spectrum contained no bands assignable to a hydroxyl function, but did show strong Si–O stretching at 1026 cm.$^{-1}$.

Mono- and Bis(1-hydroxyhexafluorocyclobutyl)phosphine.—A Carius tube containing 1.7 g. of phosphine and 8.9 g. of hexafluorocyclobutanone was allowed to stand at room temperature for 16 hr. The colorless liquid which formed in the tube was distilled to give, first, 0.6 g. of 1-hydroxyhexafluorocyclobutylphosphine, b.p. 96–97°.

Anal. Calcd. for $C_4H_3F_6OP$: F, 53.8; P, 14.6. Found: F, 53.9; P, 14.1.

The proton magnetic resonance spectrum of the primary phosphine as a neat liquid showed the OH resonance as a singlet at -3.67 p.p.m. and the PH_2 resonance as a doublet (J = 202 c.p.s.) at -2.96 p.p.m. from tetramethylsilane (external reference). When the spectrum was determined using a 50% solution in deuterioacetone (tetramethylsilane internal reference), the OH peak shifted to -6.42 p.p.m. and the PH_2 absorption to -3.20 p.p.m. Although the OH peak appeared as a clean singlet, each member of the PH_2 doublet was split into a triplet (J = 5.3 c.p.s.) because of coupling with an equivalent pair of fluorine nuclei. In addition, each member of each triplet was split into overlapping pairs of triplets ($J_{F_aH} = J_{F_bH} = 1.0 \pm 0.2$ c.p.s.) because of coupling with two other pairs of fluorines.

The F^{19} n.m.r. spectrum appeared grossly as two sets of AB patterns with an intensity ratio of 2:1. The larger set (Δ_{AB} = 10.2 p.p.m., J_{AB} = 216 c.p.s.) was centered at +60.9 p.p.m. and the smaller (Δ_{AB} = 7.3 p.p.m., J_{AB} = 229 c.p.s.) at +64.1 p.p.m. ($FCCl_2CCl_2F$ external reference). The members of both AB sets showed much additional fine structure due to coupling of the fluorine nuclei with P^{31}, H^1, and other F^{19} nuclei.

The second fraction was a clear liquid, b.p. 74.5–75.5° (8 mm.), which solidified on cooling to give colorless crystals of bis(1-hydroxyhexafluorocyclobutyl)phosphine.

Anal. Calcd. for $C_8H_3F_{12}O_2P$: F, 58.4; P, 7.94. Found: F, 58.3; P, 7.31.

Repetition of this reaction in a vacuum manifold at 25° gave immediate formation of liquid product on all the wall surfaces. Reaction of phosphine with excess fluoroketone gave a 91% yield of the crystalline secondary phosphine, m.p. 30–35°.

Boron–Phosphorus Heterocycle.—A solution of 1.55 g. of diethyl phenylboronate in 5 ml. of ether was mixed with 3.4 g. of bis(1-hydroxyhexafluorocyclobutyl)phosphine. Evaporation of the ether gave a plug of white solid. On heating to 100°, the solid melted to a clear, colorless liquid and then resolidified to give white crystals. Drying under reduced pressure removed a trace of ethanol and gave 3.0 g. of the presumed dioxaphosphaborinane (**6**), m.p. 109–110°. The solid dissolved readily in benzene and was rapidly attacked by 10% sodium hydroxide solution.

Anal. Calcd. for $C_{14}H_6BF_{12}O_2P$: C, 35.3; H, 1.27; F, 47.9; P, 6.51; mol. wt., 476. Found: C, 35.9; H, 1.73; F, 47.4; P, 6.46; mol. wt., 468.

The infrared spectrum contained bands assignable to P—H stretching (2330 cm.$^{-1}$), aromatic C=C stretching at 1500 and 1610 cm.$^{-1}$, and B—O stretching at 1330 cm.$^{-1}$ in addition to intense C—F stretching and monosubstituted aromatic bands.

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