room temperature and was heated to 50° for 4.5 hr. The reaction mixture was cooled, diluted with water, and was ether extracted. After having been washed with sodium bicarbonate solution and water and dried with magnesium sulfate, the ether solution was vacuum stripped to give 10.02 g. of crude product. Evaporative distillation at 48–58° and 0.03 mm. gave 4 ml. of colorless distillate and a thick, black residue. The distilled material in 25 ml. of ethanol was hydrogenated with a sponge nickel catalyst at 20° and 100 p.s.i.g. Filtration of catalyst and evaporation of solvent gave 2.78 g. (0.022 mole, ~22%) of a mixture of ethylcyclohexanols. The mixture was analyzed as described before.

Reaction of 1 with *t*-Butyl Peroxybenzoate.—A mixture of 1.004 g. of cuprous bromide and 50.0 ml. of 1 was stirred under helium at 70° while 2.39 g. (0.012 mole) of *t*-butyl peroxybenzoate was added over a 3.5-hr. period. Heating was continued an additional 16.5 hr., after which the mixture was cooled, filtered, washed with saturated sodium bicarbonate solution, then with water, and dried. Vacuum evaporation of unchanged olefin afforded 2.17 g. of residue.

A 2.01-g. sample was hydrogenated in ethanol with platinum oxide catalyst. This material apparently contained some unchanged olefin, since considerably more than the theoretical amount of hydrogen was absorbed (*ca.* 50% excess). The hydrogenation product was evaporatively distilled, then saponified in alcoholic sodium hydroxide. There was obtained 0.502 g. (4.0 mmoles, 36% based on total product) of ethylcyclohexanols. Analysis of the product by g.l.p.c. indicated the presence of small quantities of a number of other materials, as yet unidentified.

Acknowledgment.—The author is indebted to L. C. Jennings for much of the experimental work and to Professors W. E. Doering and R. Pettit for helpful discussions.

1-[*m*-(Ethoxydimethylsilyl)phenyl]-3-[*p*-(ethoxydimethylsilyl)phenyl]-hexafluoropropane and Its Cyclization to a Fluorinated Oxadisila-[3.3]metaparacyclophane

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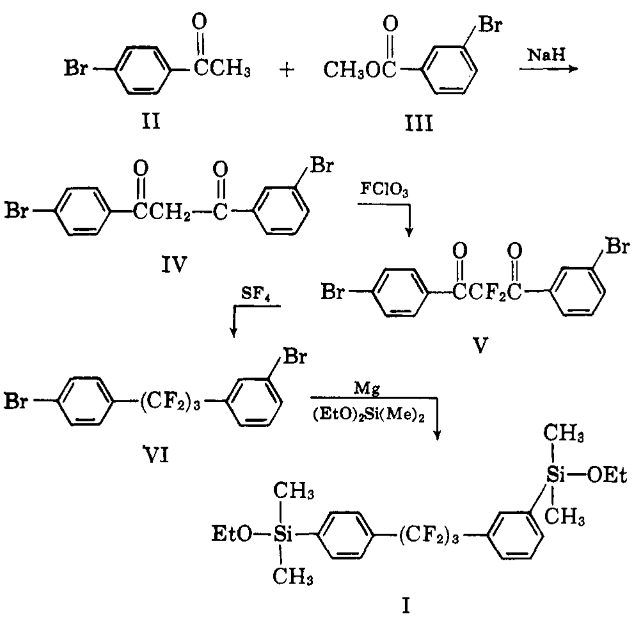
Treatment of a bifunctional Grignard compound, prepared from 1-(*m*-bromophenyl)-3-(*p*-bromophenyl)hexafluoropropane (VI) with diethoxydimethylsilane, gave 1-[*m*-(ethoxydimethylsilyl)phenyl]-3-[*p*-(ethoxydimethylsilyl)phenyl]hexafluoropropane (I). A sublimate, obtained on heating the polymer of I, was shown to be a fluorinated oxadisila[3.3]metaparacyclophane (VII). To our knowledge, this is the first metaparacyclophane to be reported. Attempts to convert 1,3-bis(*p*-bromophenyl)hexafluoropropane (X) through the bifunctional Grignard compound to 1,3-bis[*p*-(ethoxydimethylsilyl)phenyl]hexafluoropropane (VIII) were not successful.

The synthesis of 1-[*m*-(ethoxydimethylsilyl)phenyl]-3-[*p*-(ethoxydimethylsilyl)phenyl]hexafluoropropane (I) was accomplished through the following sequence.



Condensation of *p*-bromoacetophenone (II) and methyl *m*-bromobenzoate (III) with sodium hydride in benzene gave a 43% yield of 1-(bromophenyl)-3-(*p*-bromophenyl)-1,3-propanedione (IV).

Treatment of IV in pyridine with perchloryl fluoride at −10 to 10° (hazardous!)[2] resulted in a 69% yield of 1-(*m*-bromophenyl)-3-(*p*-bromophenyl)-2,2-difluoro-1,3-propanedione (V). A 53% yield of 1-(*m*-bromophenyl)-3-(*p*-bromophenyl)hexafluoropropane (VI) was obtained on treatment of V with sulfur tetrafluoride.[3] Formation of a bifunctional Grignard compound from VI, followed by reaction with excess diethoxydimethylsilane, gave a 49% yield of I.

When a solution of I in benzene was refluxed with 50% sulfuric acid, and the benzene solution washed with water and concentrated, a clear tacky polymeric gum was obtained. On heating the gum at 145–155° (0.1 mm.) over a period of 12 hr., a white crystalline sublimate was obtained in 12% yield. Resublimation gave a product, m.p. 80–81.5°, that was homogeneous by v.p.c. The empirical formula $C_{19}H_{20}F_6OSi_2$ was derived from elemental analyses and from the parent peak 434 of the mass spectrum whose base peak 419 represented loss of a methyl group. The observed intensities of the parent +1 and the parent +2 peaks were in accord with those calculated[4] for the given empirical formula. The molecular weight in benzene solution by isothermal distillation was 436. Subsequent determinations gave values of 449 and 496, indicating some repolymerization. The infrared spectrum exhibited the characteristic $Si(CH_3)_2$ band at 7.95 μ, but lacked the ethoxy C–O–Si band at 10.55 μ. The n.m.r. spec-

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[1] Deceased, September 2, 1963.

[2] Although this reaction has been carried out successfully ten times in the course of this work, it is considered to be very dangerous; all due precaution should be taken. The same procedure used in these laboratories for the fluorination of a similar compound, ethyl *p*-fluorobenzoylacetate, resulted in a violent explosion that completely demolished a 0.25-in. Plexiglas "safety" shield.

[3] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

[4] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 9.

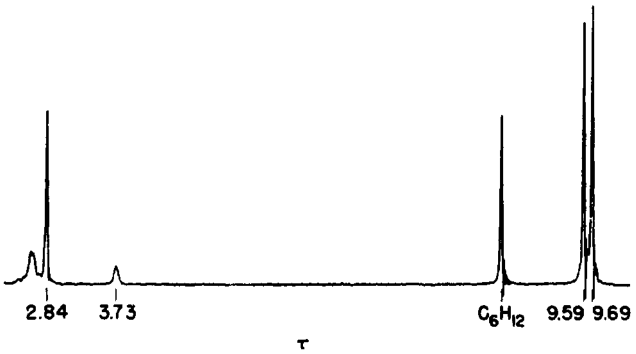
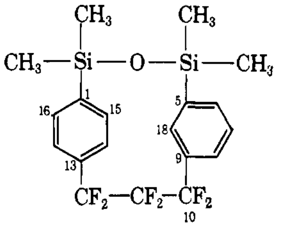


Fig. 1.—Proton n.m.r. spectrum of VII at 60 Mc.

trum (Fig. 1) showed an aromatic complex with a sharp peak at τ 2.84 ,a somewhat broadened resonance at 3.73, and two methylsilyl singlets at 9.59 and 9.69. The integrated areas for these three regions were 7.13:1.00:12.05, respectively.

From the foregoing data, the structure of a novel fluorinated oxadisila[3.3]metaparacyclophane[5] VII was assigned to this compound. To our knowledge, this is the first metaparacyclophane to be reported.[6]

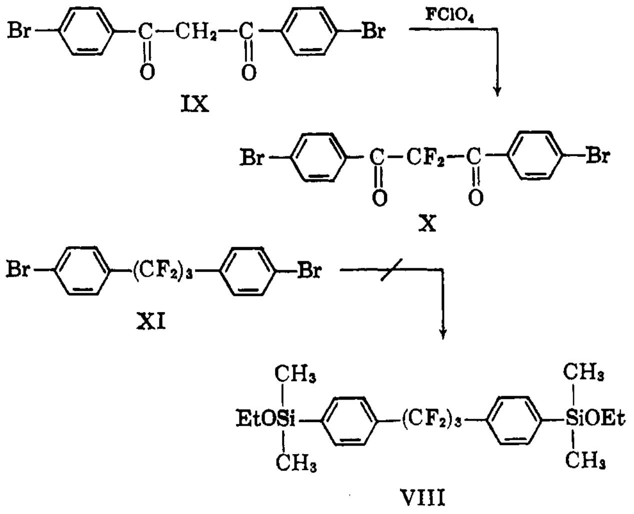


VII

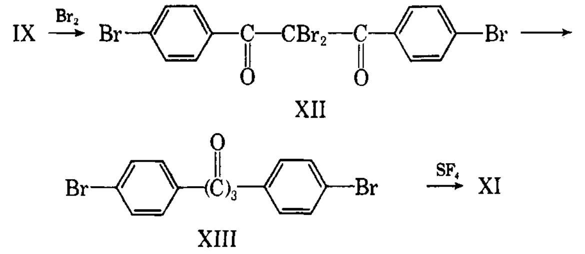
Interpretation of the n.m.r. spectrum furnished convincing evidence for the proposed structure. The τ 3.73 peak (broadened by weak *meta* and *para* coupling) was assigned to the proton between the two ring substituents in the *meta*-substituted ring (C-18). Its relatively high field shift was ascribed to the ring-current shielding effect of the *para*-substituted ring. The magnitude of the shielding was not so great as in [2.2]metacyclophane (τ 5.75)[7] because of the larger size of our [3.3]cyclophane ring.

A Stuart–Briegleb model of VII clearly illustrated this shielding. The model was rigid with an angle of approximately 25° between the ring planes; the proton on C-18 was effectively positioned over the adjacent ring. The reason for two methyl shift positions was also apparent. All four methyl groups could freely rotate, but two *cis* groups were in more highly shielded positions than the other two. It is of interest to note that VII should exist as a pair of *dl* enantiomorphs.

A sequence of reactions analogous to reactions II → I was designed to synthesize 1,3-bis[*p*-(ethoxydimethylsilyl)phenyl]hexafluoropropane (VIII). Condensation of *p*-bromoacetophenone and methyl *p*-bromobenzoate gave 1,3-bis(*p*-bromophenyl)-1,3-propanedione (IX) in 50% yield. This was converted to 1,3-bis(*p*-bromophenyl)-2,2-difluoro-1,3-propanedione (X) in 53% yield with perchloryl fluoride. The latter compound on treatment with sulfur tetrafluoride gave a 73% yield of 1,3-bis(*p*-bromophenyl)hexafluoropropane (XI). Attempts to convert this compound through a Grignard reaction with diethoxydimethylsilane to VIII under the same conditions used for conversion of VI to I were unsuccessful.



Alternative Routes.—Several other routes were explored to 1,3-bis[*p*-(ethoxydimethylsilyl)phenyl]hexafluoropropane (VIII). Bromination of 1,3-bis(*p*-bromophenyl)-1,3-propanedione (IX) by the procedure of Bigelow and Hanslick[8] gave a 79% yield of 1,3-bis-(*p*-bromophenyl)-2,2-dibromo-1,3-propanedione (XII), which was hydrolyzed in 56% yield to 1,3-bis(*p*-bromophenyl)propanetrione (XIII). Fluorination of XIV with sulfur tetrafluoride gave only a 25% yield of 1,3-bis(*p*-bromophenyl)hexafluoropropane (XI)



The method of Inman, Oesterling, and Tyczkowski,[9] using perchloryl fluoride and sodium methoxide in methanol, gave only recovered starting material when applied to the conversion of IX to X. A modification of this method, using sodium methoxide in tetrahydrofuran, gave X in 82% yield on a 5-mmole scale. However, repetition of this procedure on a tenfold larger scale gave none of the desired product. The product isolated was methyl *p*-bromobenzoate, presumably from methoxide attack on the desired product (X). An attempt to prepare 1,3-bis(*p*-bromophenyl)-2,2-difluoro-1,3-propanedione (X) from 1,3-bis(*p*-bromophenyl)-propanetrione (XIII) with potassium fluoride in dimethylformamide was unsuccessful.

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[5] Complete name by *Chemical Abstracts* nomenclature is 10,10,11,11,12,12-hexafluoro-2,2,4,4-tetramethyl-3-oxa-2,4-disilatricyclo[11.2.2.$1^{5,9}$]octadeca-5,7,9(18),13,15,16-hexaene.

[6] S. A. Fuqua and R. M. Silverstein, *Chem. Ind.* (London), 1591 (1963).

[7] D. J. Wilson, V. Boekelheide, and R. W. Griffin, *J. Am. Chem. Soc.*, **82**, 6302 (1960).

[8] L. A. Bigelow and R. S. Hanslick, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 244.

[9] C. E. Inman, R. E. Oesterling, and E. A. Tyczkowski, *J. Am. Chem. Soc.*, **80**, 6533 (1958).

Experimental

Melting points (Fisher-Johns apparatus) and boiling points are uncorrected.

Infrared spectra were recorded on either a Perkin-Elmer 221 or a Beckman IR-5; the mass spectrum on a CEC 21-103C spectrometer; the isothermal distillation molecular weight on a Mechro Labs osmometer 301.

The proton magnetic resonance spectra were obtained with a Varian HR-60 n.m.r. spectrometer operated at 60 Mc. For the silane monomers and polymers, solutions of 5–15% in carbon tetrachloride containing 1% cyclohexane were used. Shifts are reported in τ-values. A value of τ 8.56 was assigned to the cyclohexane resonance. Other proton spectra were taken in carbon tetrachloride containing 1% tetramethylsilane. The fluorine magnetic resonance spectra were obtained in trichlorofluoromethane solution and shifts are reported in parts per million from trichlorofluoromethane.

Vapor phase chromatographic analyses were performed with a 5 ft. × 0.25 in. column of 5% silicone SE-30 on Fluoropak in a Wilkens Aerograph Model A-110c. Flow rates were generally 75–85 ml./min. Retention volumes are not precisely reproducible on this instrument and are quoted only as an indication of relative peak positions.

1-(*m*-Bromophenyl)-3-(*p*-bromophenyl)-1,3-propanedione (IV).—To a stirred mixture of 430 g. (2.00 moles) of methyl *m*-bromobenzoate, 176 g. of 54.5% sodium hydride–oil dispersion (4.00 moles), and 2000 ml. of anhydrous benzene, maintained at 60° in a 12-l. flask, was added, from a dropping funnel, a solution of 398 g. (2.00 moles) of *p*-bromoacetophenone made up to 860 ml. with anhydrous benzene. One-third of the solution was added over a period of 1 hr. No reaction took place until 4 ml. of methanol was added as an initiator. Then, after an induction period of 3 hr., a brisk evolution of hydrogen started. The addition was continued over a period of 5 hr.; hydrogen evolution was monitored with a wet-test meter. Refluxing and stirring was continued overnight. The cooled mixture was treated with 60 ml. of methanol, then with a mixture of concentrated sulfuric acid and ice. Precipitated material was removed, dissolved in benzene, and added to the subsequently separated benzene layer. The benzene solution was distilled until all of the water was removed azeotropically, filtered, and cooled. Filtration gave 329 g. (43%) of crystalline material, m.p. 131–134°. Recrystallization from benzene yielded 258 g. of pure material, m.p. 138–139°; infrared, $\lambda_{\max}^{\mathrm{KBr}}$ 5.95–6.25 (broad shoulder of enolized hydrogen-bonded carbonyl), 6.30 and 6.75 (aromatic C=C), 11.92, 13.00, and 13.88 μ (aromatic ring C—H).

Anal. Calcd. for $C_{15}H_{10}Br_2O_2$: C, 47.1; H, 2.64; Br, 41.8. Found: C, 47.1; H, 2.99; Br, 41.5.

1,3-(*m*-Bromophenyl)-3-(*p*-bromophenyl)-2,2-difluoro-1,3-propanedione (V).—The apparatus used to carry out the reaction with perchloryl fluoride (hazardous, see ref. 1) was a flat-bottomed 600-ml. cylinder, 2 in. in diameter. A 9-mm. gas inlet tube was fused through the wall, as close as possible to the bottom. A coarse-frit sintered glass plate was fused circumferentially 15 mm. above the bottom. In this way, gas could be introduced below the plate, and the solution above the plate could be stirred magnetically while the entire flask was held in an ice bath. A Dry Ice–acetone condenser was attached to the neck of the cylinder (standard taper joint), and a drying tube was fitted on the vent.

In the reactor, a stirred heterogeneous mixture of 75.0 g. (0.196 mole) of (*m*-bromobenzoyl)(*p*-bromobenzoyl)methane and 250 ml. of pyridine was cooled in an ice bath and treated with perchloryl fluoride for 5 hr. at such a rate that the perchloryl fluoride (b.p. −47°) refluxed slowly and smoothly off the tip of the condenser and the reaction temperature was held at −10 to 10°. In order to maintain these conditions, perchloryl fluoride was added only periodically. The reaction mixture was then allowed to warm to 30° over 7 hr. It was poured into water and extracted with benzene. The benzene solution was washed with dilute hydrochloric acid and water, dried, and the solvent was removed at reduced pressure. Crystallization of the residue from 800 ml. of petroleum ether (b.p. 65–110°) yielded 56.6 g. (69%) of light tan crystals, m.p. 66–67°. One more recrystallization gave an analytical sample, m.p. 67.2–68°.

Anal. Calcd. for $C_{15}H_8Br_2F_2O_2$: C, 43.09; H, 1.93; Br, 38.2; F, 9.09. Found: C, 43.21; H, 1.97; Br, 38.0; F, 9.40.

1-(*m*-Bromophenyl)-3-(*p*-bromophenyl)hexafluoropropane (VI).—A mixture of 270 g. of 90% sulfur tetrafluoride (2.23 moles) and 162 g. (0.386 mole) of 1-(*m*-bromophenyl)-3-(*p*-bromophenyl)-2,2-difluoro-1,3-propanedione (V) in an 825-ml. high-pressure reactor was heated at 130° for 2 hr., at 150–170° for 12 hr., and at 225° for 7 hr. The cooled reaction mixture was dissolved in benzene and stirred with sodium fluoride. The benzene was removed, and the residue was recrystallized once from methanol–water to give 94.3 g. (53%) of light tan crystals, m.p. 53–56.5°. Fractional distillation through an 18-in. spinning-band column gave a cut, b.p. 123–125° (0.25 mm.). Recrystallization from pentane gave an analytical sample, m.p. 57–57.8°. The retention volume was 640 ml. at 180°. The proton n.m.r. spectrum consisted of an eleven-peak, complex aromatic multiplet centered at τ 2.53.

Anal. Calcd. for $C_{15}H_8Br_2F_6$: C, 39.0; H, 1.75; Br, 34.6. Found: C, 39.5; H, 1.81; Br, 34.3.

1-[*m*-(Ethoxydimethylsilyl)phenyl]-3-[*p*-(ethoxydimethylsilyl)phenyl]hexafluoropropane (I).—Magnesium turnings (4.87 g., 0.260 g.-atom), prepared from sublimed magnesium (Dow Chemical Co.), were flame-dried in a stream of dry nitrogen in a flame-dried three-necked flask, fitted with a sealed stirrer, pressure-equalizing dropping funnel, and a condenser, connected through a drying tube to a nitrogen line. A small crystal of iodine was added to the warm flask, and the magnesium was stirred in the iodine vapor. Twenty milliliters of a solution of 46.20 g. (0.100 mole) of 1-(*m*-bromophenyl)-3-(*p*-bromophenyl)hexafluoropropane (VI) in 450 ml. of tetrahydrofuran (freshly distilled from lithium aluminum hydride) was added to a refluxing mixture of the treated magnesium and 20 ml. of tetrahydrofuran. The reaction started after 10 min. The heat was removed, and the remainder of the solution of VI was added over a period of 30 min. The heat of reaction maintained reflux. Refluxing was continued for an additional hour. The homogeneous dark Grignard solution was transferred under nitrogen pressure to the dropping funnel of a similar dry apparatus, and was added over a period of 1 hr. to a refluxing mixture of 450 g. (3.03 moles) of diethoxydimethylsilane and 900 ml. of tetrahydrofuran. (Diethoxydimethylsilane was obtained from Peninsular Chemicals Research; the fraction that distilled at 113–114° through an 80-cm. helix-packed column was used.) Refluxing was continued for an additional 40 hr. Tetrahydrofuran and excess diethoxydimethylsilane were stripped and replaced with dry benzene. The precipitated salts were removed by filtration under nitrogen, and the residue was heated to 160° at 1 mm. The residue was distilled through an 8-in. spinning-band column. The desired product (27.74 g., 54.5%) distilled at 154.5–155° (0.04 mm.). V.p.c. (retention volume, 1960 ml. at 179°) showed a purity of 90%. Redistillation under the same conditions gave a product (11.85 g., $n^{25}\mathrm{D}$ 1.4750) that was 99+% pure.

The proton n.m.r. spectrum showed a methylsilyl singlet at τ 9.65, a methyl triplet at 8.85 (J = 7 c.p.s.), a methylene quartet at 6.35 (J = 7 c.p.s.), and an aromatic multiplet which consisted of a sharp intense peak arising from a broad base, most of which was at a lower field.

Anal. Calcd. for $C_{23}H_{30}F_6O_2Si_2$: C, 54.3; H, 5.94; F, 22.4; Si, 11.04. Found: C, 53.5; H, 5.76; F, 22.2; Si, 11.46.

Fluorinated Oxadisila[3.3]metaparacyclophane (VII).—A solution of 14.312 g. (28.14 mmoles, 99.5 wt. %, 98.5 mole %) of 1-[*m*-(ethoxydimethylsilyl)phenyl]-3-[*p*-(ethoxydimethylsilyl)phenyl]hexafluoropropane (I, 99 + mole % by v.p.c.) and 80.0 μl. (0.43 mmole, 0.5 wt. %, 1.5 mole %) of methylvinyldiethoxysilane (added to furnish cross-linking sites) in 50 ml. of benzene was prepared. To this solution was added a solution of 5 ml. of concentrated sulfuric acid and 10 ml. of water. The mixture was stirred and refluxed for 12 hr. Additional water and benzene were added and the benzene layer separated. The acid layer was extracted with benzene and the combined benzene solutions were consecutively washed three times with water. The solvent was removed at atmospheric pressure, then *in vacuo.* The residue was a tacky gum (ln η_r/c 0.23; c 1.1 g./dl., benzene) which weighed 12.33 g. (theoretical polymer, 12.26 g.). It was heated at 150° and 1-mm. pressure for 1 hr., during which time the viscosity increased and considerable bubbling was evident. The mixture was dissolved in benzene and transferred to another flask. The benzene was removed and the residue heated at 145–155° and 1-mm. pressure for 4 hr. During this time, white crystals sublimed into the neck of the flask. The residue in the flask was still a light amber gum. Upon removal of the sublimate and continued vacuum heating, additional white sublimate was formed. A total of 1.20 g. of crystalline white sublimate (m.p. 80–83°) was collected. The polymer residue weighed 10.99 g. Further heating of this residue yielded no more sublimate.

Resublimation gave an analytical sample, m.p. 80.0–81.5°, which was homogeneous by gas chromatography; infrared, $\lambda_{\max}^{\text{film}}$ 7.95 [$(CH_3)_2Si$], no ethoxy C–O–Si at 10.55 μ; n.m.r. (τ), 2.84 (complex with sharp peak, 7.13 protons, aromatic), 3.73 (singlet, slightly broadened, 1.00 proton, C-18), 9.59 and 9.69 (singlet, 12.05 protons, methylsilyl).

Mass spectrum. Calcd.[10] for $C_{19}H_{20}F_6OSi_2$: parent mass, 434; parent + 1 = 31.05% of parent peak ($C_{19}^{13}\,H_{20}^{2}$ = 20.85%, Si_2^{29} = 10.20%); parent + 2 = 8.98% of parent peak ($C_{19}^{13}\,H_{20}$ = 2.06%, O^{18} = 0.20%, Si_2^{30} = 6.72%). Found: parent + 1 = 31.2% of parent peak; parent + 2 = 10.4% of parent peak.

Anal. Calcd. for $C_{19}H_{20}F_6OSi_2$: C, 52.51; H, 4.64; F, 26.23; Si, 12.93. Found: C, 52.55, 52.62; H, 4.64, 4.75; F, 26.08; Si, 13.08.

1,3-Bis(*p*-bromophenyl)-1,3-propanedione (IX).—To a stirred mixture of 140 g. of 53.1% sodium hydride in oil dispersion (3.09 moles) and 323 g. (1.50 moles) of methyl *p*-bromobenzoate in 2500 ml. of dry benzene, maintained at 60°, was added, from a dropping funnel, a solution of 299 g. (1.50 moles) of *p*-bromoacetophenone made up to 500 ml. in dry benzene. Fifty milliliters of the *p*-bromoacetophenone solution was added to initiate the reaction; hydrogen evolution (wet-test meter) started in about 4 hr. The remainder of the solution was then added over a period of 4 hr., and stirring and heating were continued for an additional 10 hr. Work-up followed the procedure given for preparation of 1-(*m*-bromophenyl)-3-(*p*-bromophenyl)-1,3-propanedione (IV). A 50% yield of the crude product (m.p. 193–194°) was obtained and used without further purification in the next step. An analytical sample was obtained by recrystallization from benzene, m.p. 197–198.5°.

Anal. Calcd. for $C_{15}H_{10}Br_2O_2$: C, 47.15; H, 2.64; Br, 41.83. Found: C, 46.86; H, 2.87; Br, 41.59.

1,3-Bis(*p*-bromophenyl)-2,2-difluoro-1,3-propanedione (X).—The apparatus described above was modified by removing the condenser. A stirred mixture of 100 g. (0.262 mole) of 1-(*m*-bromophenyl)-3-(*p*-bromophenyl)1,3-propanedione (IV), and 400 ml. of pyridine was cooled to 0 to 10° (thermometer suspended in mixture) and perchloryl fluoride was slowly bubbled through for 11 hr. (hazard). The starting material slowly dissolved as the reaction proceeded. The mixture was poured into 4 l. of water, and the precipitate was removed by filtration, washed with water, and dried.

The total crude product from three runs was dissolved in hot petroleum ether (b.p. 65–110°) and filtered hot. On cooling the solution, 208 g. of product precipitated. Recrystallization from petroleum ether gave 187 g. (53%) of the desired product, m.p. 102–104°. An analytical sample obtained by an additional recrystallization melted at 105–107°. The petroleum ether-insoluble material (68.3 g.), on recrystallization from benzene, gave 42.8 g. of recovered starting material, m.p. 191–193.5°.

The infrared spectrum in a potassium bromide pellet showed the C═O absorption at 5.86, and sharp peaks at 8.62 and 8.75 μ ascribed to C—F absorption.

Anal. Calcd. for $C_{15}H_8Br_2O_3$: C, 45.5; H, 2.04. Found: C, 45.5; H, 2.16.

1,3-Bis(*p*-bromophenyl)hexafluoropropane (XI).—In an 825-ml. bomb, a mixture of 166 g. (0.396 mole) of bis(*p*-bromobenzoyl)difluoromethane and 269 g. of 90% sulfur tetrafluoride was heated at 100° for 2 hr., at 175° for 6 hr., and at 220–225° for 11 hr. Working up in the manner described for 1-(*m*-bromophenyl)-3-(*p*-bromophenyl)hexafluoropropane (VI) gave 202 g. of yellow solid which after two recrystallizations from 98% methanol yielded 133 g. (73%) of impure product (m.p. 119–123°). The high melting point of the material made distillation infeasible as a method of purification.

The product was successfully purified by column chromatography. A benzene solution of 89 g. of impure product was placed on a column of alumina 600 mm. long and 60 mm. in diameter. One fraction gave 68.1 g. of white needles (m.p. 125.0–126.0°). The fluorine n.m.r. spectrum of this material consisted of two singlets in 2:1 ratio. The larger peak, due to the four benzylic fluorine atoms, was at 109.2, and the smaller peak, due to the central CF_2, was at 122.0 p.p.m.

Anal. Calcd. for $C_{15}H_8Br_2F_6$: C, 38.99; H, 1.75; Br, 34.6. Found: C, 39.52; H, 1.81; Br, 35.5.

1,3-Bis(*p*-bromophenyl)-2,2-dibromo-1,3-propanedione (XII).—A solution of 19.2 g. (0.120 mole) of bromine in 50 ml. of chloroform was slowly added to an ice-cooled solution of 19.2 g. (0.0503 mole of 1,3-bis(*p*-bromophenyl)-1,3-propanedione (IX) in 150 ml. of chloroform at such a rate that the temperature did not exceed 15°. The hydrogen bromide evolved was removed with a stream of nitrogen. After addition of the bromine, the solution was stirred a few minutes longer. The solvent was removed at reduced pressure, and the residue was crystallized from alcohol to give 21.5 g. (79%) of white crystals (m.p. 84–88°). Three recrystallizations from absolute alcohol gave material melting at 92–94.7°; infrared, $\lambda_{\max}^{\text{film}}$ 5.92 μ.

Anal. Calcd. for $C_{15}H_8Br_4O_2$: C, 33.37; H, 1.49; Br, 59.21. Found: C, 33.72; H, 1.65; Br, 59.02.

1,3-Bis(*p*-bromophenyl)propanetrione (XIII).—A mixture of 5.4 g. (0.010 mole) of 1,3-bis(*p*-bromophenyl)-2,2-dibromo-1,3-propanedione (XII), 2.05 g. (0.025 mole) of sodium acetate, and 7.1 ml. of acetic acid was refluxed for 2 hr. The precipitate was stirred with 10 ml. of water, removed by filtration, and dried to give 4 g. of crude product. Sublimation in a vacuum and two recrystallizations from petroleum ether–benzene gave yellow needles, m.p. 145–147.5°; infrared, $\lambda_{\max}^{\text{KBr}}$ 5.92 μ.

Anal. Calcd. for $C_{15}H_8Br_2O_3$: C, 45.5; H, 2.04. Found: C, 45.5; H, 2.16.

1,3-Bis(*p*-bromophenyl)hexafluoropropane (XI) from the Triketone (XIII).—A mixture of 4.68 g. (11.8 mmoles) of 1,3-bis(*p*-bromophenyl)propanetrione (XIII) and 20 g. of 90% sulfur tetrafluoride was rocked and heated in a 100 ml. stainless steel bomb for 7 hr. at 50° and 8 hr. at 150° (250 p.s.i.). The product was dissolved in benzene and washed with dilute sodium bicarbonate solution. The benzene solution was filtered through a short alumina column and allowed to crystallize to give 1.38 g. (25%) of crude product (m.p. 114–121°). Several recrystallizations from benzene gave white crystals (m.p. 120–122°).

Anal. Calcd. for $C_{15}H_8F_6Br_2$: C, 38.99; H, 1.75. Found: C, 38.91; H, 1.87.

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(10) Silicon isotope abundances recalculated on basis Si^{28} = 100% from L. A. Koenig, J. H. E. Mattauck, and A. H. Wapstra, *Nucl. Phys.*, **31**, 18 (1962).