g (12.8 mmoles) of XIV afforded 200 mg (10%) of the dimer XVI and 300 mg (15%) of the starting material XIV in the step before the chromatography. In the chromatography, the evaporation of eluted benzene–petroleum ether (1:1) fraction gave 300 mg (15%) of a ketal XVIII as colorless needles: mp 72° (after recrystallization from petroleum ether); λ_{max}^{MeOH} end absorption at 210 mμ; ν_{max}^{KBr} 2994, 1754 cm^{-1}; nmr, τ 6.1–8.0 (C_1, C_4, C_5H and CH_2 of ethyl, m, 8 H), 4.18 (C_7H, d, 1 H), 8.70 and 8.81 (CH_3 of ethyl, t, 6 H) with $J_{1,7} < 1.0$[19] and $J_{CH_3CH_2} = 6.6$ cps.

Anal. Calcd for $C_{11}H_{15}O_3Cl$: C, 57.37; H, 6.55. Found: C, 57.71; H, 6.51.

Elution with benzene–ether (9:1) afforded 95 mg (5%) of XIX as colorless needles: mp 42° (after recrystallization from petroleum ether); λ_{max}^{MeOH} 273 mμ (log ϵ 4.15); ν_{max}^{KBr} 1724 (ester), 1706 (cyclopentenone), 1642 cm^{-1}; nmr, τ 2.20 (C_2H, d, 1 H), 3.43 (C_3H, d, 1 H), 6.59 (C_5H, d, 2 H), 3.98 (side-chain H, t, 1 H), 5.72 and 8.69 (OC_2H_5, q and t, 5 H) with $J_{2,3} = 4.8$, $J_{5,6} = 2.0$, and $J_{CH_3CH_2} = 6.6$ cps.

Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 64.91; H, 6.39.

From the eluted ether solution, 60 mg (3%) of XI as colorless needles, mp 103°, was obtained (after recrystallization from benzene–cyclohexane, 1:9).

Hydrolysis of 2,2-Dimethoxy- (XV) and 2,2-Diethoxy-6-chloro-Δ^6-bicyclo[3.2.0]hepten-3-one (XVIII). **A.**—To a mixture of 2 ml of dioxane and 3 ml of 0.5 *N* hydrochloric acid, 150 mg (0.7 mmole) of XV was added and the resulting solution was heated on a boiling-water bath for 1 hr. The solution was poured into 20 ml of water and extracted with ether. The ether extract was washed with water, dried over sodium sulfate, and evaporated to give 125 mg of an orange oil as residue. When 2 ml of benzene was added to the oil, crystals separated and 45 mg of colorless needles, mp 99–102°, was obtained by filtration. Evaporation of the filtrate afforded 80 mg of an orange oil, which, on distillation under 2 mm in an oil bath heated at 70–80°, gave 30 mg of colorless needles, mp 100–102°. The combined crystals, mp 103° (65 mg, 57%, after recrystallization from benzene–cyclohexane), were proved to be identical with XI by the mixture melting point determination and by comparison of the infrared spectra.

B.—Compound XVIII (200 mg, 0.9 mmole) was dissolved in a mixture of 4 ml of 0.5 *N* hydrochloric acid, 2 ml of ethanol, and 0.5 ml of dioxane. The solution was treated in the same manner as described in A, giving 140 mg of pale yellow crystals which, on sublimation at 70–80° under 2 mm, afforded 75 mg (54%) of XI as colorless needles, mp 103° (after recrystallization from benzene–cyclohexane).

Decomposition of the Dimer XVI to the Monomer XI.—To a mixture of each 2 ml of dioxane and water and 1 ml of 5% aqueous sodium hydroxide solution, 50 mg (0.16 mmole) of XVI was dissolved. The resulting solution was allowed to stand overnight at room temperature, during which time it became red. The solution was acidified by addition of dilute hydrochloric acid and extracted with chloroform. The chloroform extract was washed with water, dried over sodium sulfate, and evaporated to give 35 mg (70%) of XI as colorless needles, mp 103° (after recrystallization from benzene–cyclohexane). A solution of 50 mg (0.16 mmole) of XVI dissolved in each 2 ml of dioxane and 6 *N* hydrochloric acid was heated on a boiling-water bath for 2 hr when, however, XVI was recovered in a quantitative yield.

Irradiation of 6-Chloro-3-hydroxy-$\Delta^{3,6}$-bicyclo[3.2.0]heptadien-2-one (XI).—A solution of 30 mg (0.2 mmole) of XI in 6 ml of ethanol was placed in Pyrex tube and flushed with pure nitrogen for 5 min. After the tube had been sealed, the solution was irradiated externally with the Toshiba H-400P lamp placed 20 cm from the tube. After 15 hr of irradiation, the absorption maxima around 271 mμ of XI disappeared. Evaporation of the solution afforded 25 mg (80%) of colorless needles, mp 235° (after recrystallization from chloroform), which were identical with the dimer XVI.

Reaction of the Dimer XVI with Phosgene.—To a solution of 80 mg (0.25 mmole) of XVI in 3 ml of chloroform and 3 ml of pyridine, 8 ml of a toluene solution containing 40% phosgene was added. After the resulting solution had been allowed to stand at room temperature for 2 days, it was added to 30 ml of water to decompose the excess phosgene. The organic layer separated, was washed with water, dried over sodium sulfate, and evaporated under reduced pressure to give 72 mg (85%) of colorless crystals, mp 255°. Recrystallization from benzene–ether (1:5) afforded carbonate XVII as colorless needles: mp 255°; ν_{max}^{KBr} 1869, 1852, and 1789 cm^{-1}; mass spectrum (*m/e*) 340 and 338 (molecular ion).

Anal. Calcd for $C_{15}H_8O_5Cl_2$: C, 53.12; H, 2.38. Found: C, 53.42; H, 2.70.

Methylation of 6-Chloro-3-hydroxy-$\Delta^{3,6}$-bicyclo[3.2.0]heptadien-2-one (XI).—A few bubbles of hydrogen chloride gas were flushed through a solution of 25 mg (0.16 mmole) of XI dissolved in 3 ml of methanol. The resulting solution was allowed to stand in the dark at room temperature for 2 hr. The evaporation of the solution afforded 30 mg of a dark red oil which was dissolved in benzene–cyclohexane (1:2) and the solution was chromatographed on alumina (activity III, 1 g). Evaporation of eluted benzene solution gave 15 mg (35%) of a colorless oil, which was proved to be identical with ketal XV by comparison of the infrared spectrum. Elution with benzene–ether followed by evaporation afforded 10 mg (33%) of colorless crystals, mp 63° (after recrystallization from cyclohexane), which were found to be identical with III by the mixture melting point determination.

Registry No.—I, 13187-38-7; II, 13168-79-1; III, 13168-80-4; IV, 13187-39-8; V, 13168-81-5; VI, 13168-82-6; 2,4-dinitrophenylhydrazone of VII, 13168-83-7; 2,4-dinitrophenylhydrazone of VIII, 13168-84-8; X, 13168-85-9; XI, 13168-86-0; XIV, 3084-17-1; XVa, 13168-87-1; XVIa, 13168-88-2; XVII, 13168-89-3; XVIII, 13168-90-6; XIX, 13296-18-9.

Synthesis of Terminal Perfluoromethylene Olefins

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A novel class of potential monomers, 1,1-difluoro-2-di- and -trihalomethylalk-1-enes, has been synthesized. The reaction of lithium aluminum hydride with the highly halogenated olefins $RHC{=}C(CF_2X)_2$, where R is hydrocarbon or hydrogen and X is Cl or F, results in the formation of terminal perfluoromethylene olefins of the general type $CF_2{=}C(CF_2X)R'$, where R′ is hydrocarbon and X is F, Cl, or H. An S_N2' reaction is believed to be involved in the synthesis. Concentration of reagents, mode of addition, and reaction temperature all affect the product yield, which varies from 43 to 84%. For example, a 65% yield of $CF_2{=}C(CF_2H)CH_3$ results from the reaction of 1 mole of $CH_2{=}C(CF_2Cl)_2$ with 2 moles of lithium aluminum hydride in ether at 0°.

Terminal perfluoromethylene olefins of the general type $CF_2{=}C(CF_2X)R'$, where R′ is a hydrocarbon group and X is F, Cl, or H, may offer unique properties when polymerized. With a view toward ultimately studying such polymers, a program of synthesis of the monomeric precursors was undertaken.

Although a number of synthetic routes for the preparation of 1,1-difluoro-2-trifluoromethylprop-1-ene (I)

TABLE I

PRODUCTS OF REACTION OF 1,1-DI(PERHALOMETHYL)ALK-1-ENES WITH LITHIUM ALUMINUM HYDRIDE

Compd	Compound	Formula	Bp (mm), °C	$n^{25}D$	Yield, %
VIII	1,1-Difluoro-2(trifluoromethyl)prop-1-ene	$C_4H_3F_5$	11–12.5[a]	...	84
IX	1,1-Difluoro-2(difluoromethyl)prop-1-ene	$C_4H_4F_4$	19–20	...	65
X	1,1-Difluoro-2(chlorodifluoromethyl)prop-1-ene	$C_4H_3ClF_4$	44–46	1.3338	75
XI	1,1-Difluoro-2(trifluoromethyl)but-1-ene	$C_5H_5F_5$	31.5–32	1.2990	43
XIII	1,1-Difluoro-2(trifluoromethyl)oct-1-ene	$C_9H_{13}F_5$	47–48 (32)	1.3568	62

[a] Lit. bp 13.8°,[1] 12–13°,[2] 12.8–13.5°.[3]

have been reported,[1–3] the methods used are tedious and the yields are poor. Except for the above compound, it appears that 1,1-difluoro-2-di- and -trihalomethylalk-1-enes, as a class, are unknown. The highly halogenated olefins $RHC{=}C(CF_2X)_2$, where R is hydrocarbon or hydrogen and X is Cl or F, appeared to be attractive starting materials for terminal perfluoromethylene olefins of the general type $CF_2{=}C(CF_2X)R'$, where R′ is hydrocarbon and X is F, Cl, or H. The olefins, $RHC{=}C(CF_2X)_2$, are obtained in good yield *via* the Grignard reaction with highly halogenated ketones followed by phosphorous pentahalide treatment of the resultant alcohols.[4]

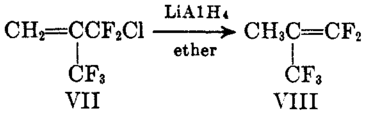
Our early efforts to convert the precursor olefins to the desired products were hampered by competing reactions. Low yields and intractable mixtures generally resulted, making normal work-up and product characterization impossible. These unsuccessful routes, however, provided clues which led to a suitable synthesis of the desired class of 1,1-difluoro olefins.

Upon infrared and nmr examination of the mixture of products obtained from platinum black and rhodium-alumina-catalyzed hydrogenation of the precursor olefins, we obtained evidence of the presence of $CF_2{=}$ containing compounds. Similar evidence was obtained from investigation of the mixed products from the reaction of 1,1-di(chlorodifluoromethyl)ethylene (II) with sodium iodide when a double S_N2' reaction[5] to form 1,1-difluoro-2-(difluoroiodomethyl)-3-iodoprop-1-ene (III) was attempted.

When II was passed through a hot quartz tube, extensive decomposition occurred. Nmr examination of the mixed products revealed spectra characteristic of the $CF_2{=}$ group; however, yields were very low.

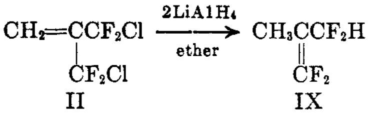
In attempts to form 1,1-di(chlorodifluoromethyl)-1-bromoethane (IV) and 1,1-di(chlorodifluoromethyl)-1-iodoethane (V) for dehalogenation reactions, reduction of 1,1-di(chlorodifluoromethyl)-1,2-dibromoethane (VI) *via* Grignard reagents resulted in starting olefin. Treatment of the olefin with hydroiodic acid resulted in extensive decomposition. Upon infrared examination of the mixed products obtained from the latter reaction, we observed absorption bands characteristic of the $CF_2{=}$ group.

The reaction of $RHC{=}C(CF_2X)_2$, where R is hydrogen or hydrocarbon and X is Cl or F, with lithium aluminum hydride in ether or tetrahydrofuran was found to give good yields (*cf.* Table I) of terminal perfluoromethylene olefins. Thus 3-chloro-3,3-difluoro-2(trifluoromethyl)prop-1-ene (VII) is converted to 1,1-difluoro-2-trifluoromethylprop-1-ene (VIII) at 0° in about 84% yield (eq 1). It appears plausible that an S_N2' reaction[5] is involved. In the performance of these allylic displacement reactions, it was found that reaction conditions have a great effect on the course of the reaction and the product yield. In the case of single displacements, as shown in eq 1, yields are greatest when (a) the molar ratio of lithium aluminum hydride to starting olefin is 0.5, (b) an ether solution of the hydride is added to an ether solution of the olefin, and (c) the temperature is kept at −5 to 5°.



$$\begin{array}{lcl} CH_2{=}CCF_2Cl & \xrightarrow[\text{ether}]{LiAlH_4} & CH_3C{=}CF_2 \\ \quad | & & \quad | \\ \quad CF_3 & & \quad CF_3 \\ \quad \text{VII} & & \quad \text{VIII} \end{array} \qquad (1)$$

In double displacement reactions, order of addition of the reagents does not significantly affect the yield, although a molar ratio of hydride to olefin of 2.0 and a reaction temperature of −5–5° is necessary to obtain good yields of double displacement products, *e.g.*, in the formation of 1,1-difluoro-2-(difluoromethyl)prop-1-ene (IX) from II (eq 2). Where a double displacement is possible, but only the first displacement is desired, a maximum yield of product occurs when the hydride to olefin molar ratio is kept at 0.5 and the temperature is kept at 10° or less. However, if the reaction temperature is kept near −70°, a ratio >0.5 can be tolerated, but with significantly less yield.



$$\begin{array}{lcl} CH_2{=}CCF_2Cl & \xrightarrow[\text{ether}]{2LiAlH_4} & CH_3CCF_2H \\ \quad | & & \quad \| \\ \quad CF_2Cl & & \quad CF_2 \\ \quad \text{II} & & \quad \text{IX} \end{array} \qquad (2)$$

Experimental Section[6]

Preparation of 1,1-Difluoro-2-(trifluoromethyl)prop-1-ene (VIII).—In a typical run, 362 g (2.0 moles) of dry VII was dissolved in 1 l. of anhydrous ether in a dry 2-l., three-necked, round-bottomed flask fitted with a magnetic stirring apparatus, thermometer, inert atmosphere inlet, dropping funnel, and exit tube leading to a 1-l. cold trap. The solution was maintained at −5 to 5° under a dry nitrogen atmosphere. Over a 90-min period, a 20% ethereal solution containing 37.9 g (1.0 mole) of lithium aluminum hydride was added. A white precipitate formed immediately. When addition was complete, stirring was continued at room temperature for 1 hr. The thermometer and dropping funnel were than replaced with glass stoppers and the suspension was cooled to −70°. By lowering the pressure to 10 mm, sealing the apparatus, and warming the suspension, the liquids were distilled into the cold trap. Distillation to dryness was avoided because of possible explosive decomposition of the dry residue. Fractionation of the crude distillate on a 4-ft concentric-tube column with refrigerated coolant gave 293 g (83.5%

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yield) of VIII, bp 11–12.5°. Infrared bands were obtained at 2860–3000 (CH_3, weak), 1740–1790 ($C{=}CF_2$, strong), and 1075–1160 cm^{-1} (C–F, strong). Structure was confirmed by nmr: fluorine spectra at 56.4 Mcps = 64.2 ppm (CF_3, quartet), 80.3 ppm ($C{-}F_2$, complex multiplet, *trans* to CF_3), 84.7 ppm ($C{-}F_1$, complex multiplet *cis* to CF_3) with trichlorofluoromethane as internal reference; proton spectra at 60 Mcps = 8.22 τ (CH_3, triplet) with tetramethylsilane as internal reference.

Preparation of 1,1-Difluoro-2-(chlorodifluoromethyl)prop-1-ene (X).—The same experimental procedure given for VIII was followed. To a cold (−70°) stirred solution of 4.75 g (0.125 mole) of lithium aluminum hydride dissolved in 200 ml of dry tetrahydrofuran was added, over a 20-min period, 49.2 g (0.25 mole) of dry II in 50 ml of dry tetrahydrofuran. Fractionation of the resultant liquid gave 22.9 g (56% yield) of X, bp 42–44°. Structure was confirmed by nmr. When the above reaction was repeated at a reaction temperature of −10°, the yield of product, bp 42–44°, rose to 75% of theory. Vapor phase chromatography[7] (vpc) was used to purify samples for elemental analysis and refractive index. Infrared bands were obtained at 2860–3000 (CH_3, weak), 1740–1780 ($C{=}CF_2$, strong), 1060–1150 (C–F, strong), and 685 cm^{-1} (C–Cl, medium).

Anal. Calcd for X ($C_4H_3ClF_4$): C, 29.55; H, 1.86; Cl, 21.81; F, 46.76. Found: C, 29.70; H, 1.87; Cl, 21.59; F, 46.86.

Preparation of 1,1-Difluoro-2-(difluoromethyl)prop-1-ene (IX).—The equipment and technique used were generally the same as for VIII. A 20% lithium aluminum hydride–diethyl ether solution (103.5 ml, 0.50 mole of $LiAlH_4$) diluted with 100 ml of dry diethyl ether was treated with 49.2 g (0.25 mole) of dry II diluted with 100 ml of dry diethyl ether over a 2-hr period, with stirring, at 0–10°. The yield of IX, bp 19–20°, was 20.8 g, which is 65% theory. Vpc was used to purify an analytical sample. Infrared bands were obtained at 2850–3000 ($-CH_3$, medium), 1750–1780 ($C{=}CF_2$, strong), and 1030–1090 cm^{-1} (C–F, strong). Structure was confirmed by nmr: fluorine spectra at 56.4 Mcps = 118.1 ppm (CF_2H, pair of doublets), 89.6 and 88.2 ppm ($C{-}F_2$, *cis* to CF_2H, and $C{-}F_1$, *trans* to CF_2H, respectively; AB quartet, $J_{AB} = 42$ cps) with trichlorofluoromethane as internal reference; proton spectra at 60.0 Mcps = τ 8.30 (CH_3, complex multiplet) and τ 3.62 (CF_2H, 55 cps, triplet); with tetramethylsilane as internal reference.

Anal. Calcd for IX ($C_4H_4F_4$): C, 37.51; H, 3.14; F, 59.34. Found: C, 37.60; H, 3.21; F, no consistent values.

Preparation of 1,1-Difluoro-2-(trifluoromethyl)but-1-ene (XI).—Dry 1-trifluoromethyl-1-(chlorodifluoromethyl)prop-1-ene (XII) (97.3 g, 0.5 mole) in 100 ml of dry tetrahydrofuran was treated at 5° with 4.75 g (0.125 mole) of lithium aluminum hydride dissolved in 100 ml of dry tetrahydrofuran. The technique used was the same as for VIII. The yield of XI, bp 31.5–32°, was 29.5 g, a 43% yield. Infrared bands were obtained at 2860–3000 (saturated C–H, medium), 1725–1760 ($C{=}CF_2$, strong), and 1100–1150 cm^{-1} (C–F, strong). Structure was confirmed by nmr: fluorine spectra at 56.4 Mcps = 63.3 ppm (CF_3 quartet), 79.2 ppm ($C{-}F_2$, complex multiplet, *trans* to CF_3), 84.6 ppm ($C{-}F_1$, complex multiplet, *cis* to CF_3) with chlorotrifluoromethane as internal reference; proton spectra at 60 Mcps = τ 8.86 (CH_3 triplet), τ 7.77 (CH_2) with tetramethylsilane as internal reference.

Anal. Calcd for XI ($C_5H_5F_5$): C, 37.51; H, 3.15; F, 59.34. Found: C, 37.68; H, 3.33; F, 59.06.

Preparation of 1,1-Difluoro-2-(trifluoromethyl)oct-1-ene (XIII).—A dry, 250-ml, three-necked, round-bottomed flask fitted as for VIII was charged with 40.2 g (0.157 mole) of dry 1-trifluoromethyl-1-(chlorodifluoromethyl)hept-1-ene (XIV) in 80 ml of dry diethyl ether. The solution was cooled to 0° and 16.3 ml (0.078 mole) of 20% lithium aluminum hydride in diethyl ether was introduced over a 15-min period with stirring. A white precipitate formed almost at once. Upon complete addition, the suspension was stirred at room temperature for 20 min and then cooled to −180° with liquid nitrogen. A 0.5–1-mm pressure was established in the pot and cold trap and the apparatus was sealed off. The pot contents were then rewarmed and distilled into the cold trap. Fractionation of the trap contents on a 2-ft spinning-band column yielded 21.3 g (a 61.5% yield) of XIII, bp 47–48° (32 mm). Infrared bands were obtained at 2850–3000 (saturated C–H, strong), 1725–1755 ($C{=}CF_2$, strong), and 1100–1150 cm^{-1} (C–F, strong).

Anal. Calcd for XIII ($C_9H_{13}F_5$): C, 50.00; H, 6.06; F, 43.94. Found: C, 50.16; H, 6.13; F, 44.09.

Registry No.—VIII, 2253-00-1; IX, 13369-09-0; X, 13395-59-0; XI, 13369-10-3; XIII, 13369-11-4.

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(7) A 3/8 in. × 20 ft aluminum vpc column, packed with Chromasorb W impregnated with 30% by weight of SE-30 (Aerograph methylsilicone gum ubber).

Purine Nucleosides. XV. The Synthesis of 8-Amino- and 8-Substituted Aminopurine Nucleosides[1]

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The direct bromination of 2′-deoxyguanosine to furnish 8-bromo-2′-deoxyguanosine has been accomplished and treatment of xanthosine under similar reaction conditions with saturated bromine–water has provided a new and direct preparation of 8-bromoxanthosine. Nucleophilic displacement of bromine from 8-bromoxanthosine, 8-bromoguanosine, 8-bromoinosine, 8-bromo-2′-deoxyadenosine, 8-bromoadenosine, and 8-bromo-2′-deoxyguanosine has provided the corresponding 8-amino- and 8-substituted aminopurine ribonucleosides. Possible biochemical significance of these nucleosides is discussed. The application of proton magnetic resonance spectroscopy for the assignment of anomeric configuration to 2′-deoxyribofuranosyl nucleosides is discussed.

Halogenation has been shown[2-6] to produce significant biochemical modifications of certain nucleic acids and has prompted the synthesis[7-10] of several 8-halogenated purine nucleosides and their derivatives.

8-Aminoguanosine and 8-aminoadenosine have demonstrated effective inhibition of a *Streptococcus faecalis*

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