1,1,3,4,4-Pentaphenyl-3-buten-1-ol (XIV).—A 175-ml. solution of 2 g. of the unsaturated ketone XIII[6b] (isomeric with VIII) was added dropwise to a stirred 125-ml. ether solution of phenylmagnesium bromide (from 1.22 g. of Mg). After refluxing for 2.5 hr. and standing for 8 hr., work-up was by hydrolysis in ammonium chloride, drying the ether extract, and evaporating. The resulting solid was crystallized from ethanol (with charcoal treatment): yield 1.47 g. (61%) of XIV, needles, m.p. 177.5–178°, infrared (hydroxyl) 3500 cm.$^{-1}$.

Anal. Calcd. for $C_{34}H_{28}O$: C, 90.23; H, 6.24. Found: C, 90.20; H, 6.36.

A small sample of XIV was converted by boiling concentrated HCl–AcOH into the diene XII (identified).

1,1,2,4,4-Pentaphenylbutadiene-1,3 (XII).—The total crude solid obtained above from 2 g. of XIV was treated briefly with hot of concentrated HCl–AcOH mixture (25:100). Pouring into water, neutralizing the acid, and ether extraction, gave 1.36 g. (56%) of the diene XII, needles from absolute ethanol: m.p. 172.5–173.5°; λ_{max} (ethanol) 240 and 342 mμ (ϵ 24,890 and 16,950); infrared aromatic C–H band, 3170 cm.$^{-1}$, no absorption at 1660–2800 cm.$^{-1}$.

Anal. Calcd. for $C_{34}H_{26}$: C, 93.96; H, 6.03. Found: C, 93.79; H, 5.77.

Raney Nickel Hydrogenation of 1,1,4,4-Tetraphenylbutyne-1,4-diol[7a] (XVIII).—In repetition of the work of Cadiot and Chodkiewicz,[7a] 10 g. of catalyst was prepared from Raney nickel by heating (steam bath) with 100 ml. of 40% sodium hydroxide (1.5 hr.) and washing finally with absolute ethanol (ignited paper upon drying). Hydrogenation of 1 g. of XVIII in ethanol–benzene mixture (0.2 g. of catalyst) at 30 p.s.i. at 30°, and fractional crystallization of the solid products from carbon disulfide and petroleum hexane, yielded 40% of *cis* dicarbinol IX,[7] m.p. 100.5–102° (corresponding to "α-isomer" of Cadiot and Chodkiewicz[7a]) which showed a broad infrared hydroxyl band at 3500 and no absorption at 2880–1570 cm.$^{-1}$. The higher melting product, m.p. 203.5–205.5° (23%, corresponding to the "β-isomer" of Cadiot and Chodkiewicz[7a]), was identified as the saturated 1,4-glycol, 1,1,4,4-tetraphenylbutane-1,4-diol, by mixture melting point and infrared analysis with an authentic sample prepared by addition of phenylmagnesium bromide to diethyl succinate[12] (infrared hydroxyl band at 3600 cm.$^{-1}$). Evidently the "β-isomer" (of Cadiot and Chodkiewicz[7a]), supposed to be the *trans* diol VI, is the result of completion of hydrogenation to the saturated glycol, and the supposed isomerization of the "α-isomer" (*cis* IX) is due rather to reduction by hydrogen absorbed on the catalyst.

A New Preparation of 1,1,4,4-Tetraphenylbutyne-1,4-diol (XVIII).—To phenyllithium from 9.2 g. (1.31 g.-atoms) of lithium in 150 ml. of ether, was added dropwise 10 ml. of acetylene dicarbomethoxylate in 50 ml. of ether in a Dry Ice–acetone bath. Work-up and crystallization from isopropanol (with charcoal treatment) gave a total of 8.1 g. (33%) of the glycol XVIII (identified by comparison with a sample prepared by the addition of phenyllithium to dibenzoylacetylene).[14a]

Lithium Aluminum Hydride Reduction of Tetraphenylbutyne-1,4-diol (XVIII).—To an ether slurry of 1.52 g. (0.04 mole) of lithium aluminum hydride in 250 ml. of absolute ether was added 5 g. (0.013 mole) of XVIII portionwise over 4 min., followed by refluxing 3.5 hr. After hydrolysis and work-up the resulting solid was crystallized from ethanol, 1.13 g. (25%) of 1,1,4,4-tetraphenylbutadiene-1,3 (XII). This was identified by correspondence to known properties,[17] unusual melting behavior (m.p. 195.5–197°, resolidifying, and clearing up at 203°), analysis, blue fluorescence under ultraviolet light, and λ_{max} (ethanol) 250 and 342.5 mμ (ϵ 22,240 and 35,550). From the filtrate from XII (above) 2.81 g. (61%) of nearly pure *trans* ethylenic glycol XI crystallized, m.p. 198–202.5° (identified by mixture melting point with an authentic sample[6]).

A similar experiment on a sample of the saturated glycol, 1,1,-4,4-tetraphenylbutane-1,4-diol, involved evolution of hydrogen, but upon work-up starting material was recovered (90%, identified).

In a preliminary experiment, $NaBH_4$ in absolute ethanol (refluxing for 4 hr.) did not appear to reduce the acetylenic glycol XVIII.

Failure of Lithium Aluminum Hydride to Reduce Tetraphenylbutatriene (Tetraphenylcumulene).—To a solution of 322 mg. of $LiAlH_4$ in 50 ml. of dry ether was added 1 g. of tetraphenylcumulene[16] (4-hr. reflux, under N_2). Hydrolysis and extraction by 200 ml. of ether gave 0.98 g. (98%) of starting material (m.p. 235–237°, identified).

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[17] K. B. Alberman, R. N. Hazeldine, and F. B. Kippling, *J. Chem. Soc.*, 3284, 1952.

The Exchange Reactions of Fluorinated Cyclobutenes with Grignard Reagents

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Certain fluorinated cyclobutenes have been found to undergo a "halogen–metal exchange" with Grignard reagents in the following manner where A is Br and B is Cl or Br, and also where A is I and B is Br. However,

if A is bromine and B is fluorine, a competing reaction was also observed to take place. The cyclobutenyl Grignard reagent in which B is chlorine was found to undergo rearrangement. Reaction of the cyclic Grignard reagent with water and with elemental iodine gave hydrogen- and iodine-substituted cyclobutenes, respectively, in good yields. Various reaction products were isolated and identified and these products are thought to arise *via* an S$_N$2′ reactions involving the Grignard reagent.

Only a few examples of "halogen–magnesium interchange" reactions have been reported in the literature[1] and of these only one has involved exchange of vinylic halogen. Knunyants[2] has shown that iodotrifluoroethylene, when treated with phenylmagnesium bromide, undergoes this type of exchange to give the vinyl Grignard reagent, $CF_2{=}CFMgBr$.

In contrast to the exchange reaction, fluoro olefins containing only fluorine or chlorine atoms at the vinylic position are known to undergo a substitution reaction with Grignard reagents at the vinylic position.[3] Park and Fontanelli[4] have extended this reaction to fluorinated cyclobutene compounds.

The preparation of a fluorinated vinyl Grignard reagent was first reported by Park, Seffl, and Lacher[5] in the reaction of $CF_2{=}CFI$ with magnesium in ether. In 1956, Gray[6] reported the reaction of $CF_2{=}CBr_2$

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[1] For references, see W. Reeve and L. W. Fine, *J. Am. Chem. Soc.*, **86**, 880 (1964).

[2] R. N. Sterlin, L. N. Pinkins, I. L. Knunyants, and L. F. Nezgovorov, *Khim. Nauka i Promy.*, **4**, 809 (1959); *Chem. Abstr.*, **54**, 10837 (1960).

[3] P. Tarrant and D. A. Warner, *J. Am. Chem. Soc.*, **76**, 1624 (1959).

[4] J. D. Park and R. Fontanelli, *J. Org. Chem.*, **28**, 258 (1963).

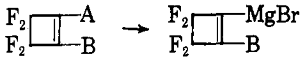
[5] J. D. Park, R. J. Seffl, and J. R. Lacher, *J. Am. Chem. Soc.*, **78**, 59 (1956).

[6] D. N. Gray, Ph.D. Thesis, University of Colorado, 1956.

with magnesium in tetrahydrofuran to give the Grignard reagent, $CF_2{=}CBrMgBr$, and, in 1958, Park, *et al.*,[7] reported the preparation of $CF_2{=}CBrMgI$ and $CF_2{=}CClMgI$ by the reaction of $CF_2{=}CBrI$ and $CF_2{=}CClI$, respectively, with magnesium in ether. Until now, no report of a fluorinated cyclobutenyl Grignard reagent has appeared in the literature.

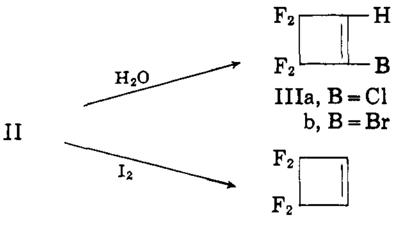
For this work, a series of fluorinated cyclobutenes was prepared in which the relative ability of various vinylic halogens to undergo substitution and exchange reactions could be studied.

The preparation of the cyclic Grignard reagent II was accomplished by reaction of the vinylic bromine or iodine of I with ethylmagnesium bromide in ether. Hydrolysis of II was found to give III in good yield and treatment of II with iodine gave IV.



I II

Ia, A = Br; B = Cl IIa, B = Cl
b, A = Br; B = Br b, B = Br
c, A = I; B = Br



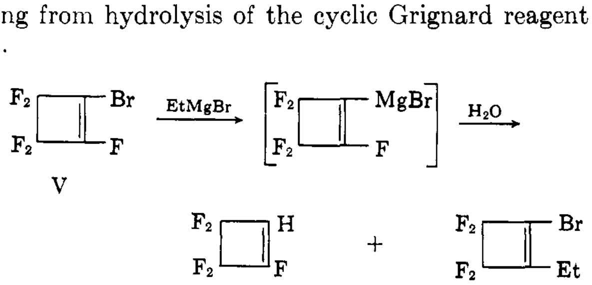
IIIa, B = Cl
b, B = Br

IVa, B = Cl
b, B = Br

In order to determine that the hydrogen in III had arisen by reaction of II with water and not by a reductive action of ethylmagnesium bromide on I with the production of ethylene, I was treated with both methyl and phenylmagnesium bromide. In each case, after addition of water, the same product (III) resulted.

In the reactions of Ib and Ic with ethylmagnesium bromide, no trace of hydrolysis product which would result from formation of a di-Grignard reagent was detected by v.p.c. analysis.

The reaction of 1-bromo-2,3,3,4,4-pentafluorocyclobutene (V) with ethylmagnesium bromide was observed to give a small amount of 1-bromo-2-ethyl-3,3,4,4-tetrafluorocyclobutene (VII), in addition to the product resulting from hydrolysis of the cyclic Grignard reagent (VI).



V VI VII

The exchange reaction involving vinylic bromine was found not to be successful in certain cyclobutenes containing a vinylic hydrogen or a vinylic ethoxy group. For example, 1-bromo-3,3,4,4-tetrafluorocyclobutene (IIIb) and 1-ethoxy-2-bromo-3,3,4,4-tetrafluorocyclobutene were each found to undergo a rapid, mildly exothermic reaction with ethylmagnesium bromide, but the only product isolated was a mixture of high-boiling hydrocarbons.

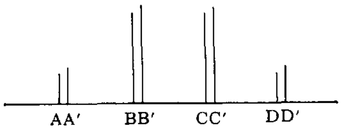
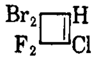
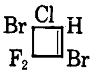


Fig. 1.—F^{19} n.m.r. spectrum of IX. A is at 5667 c.p.s. using trichloromethane as reference; J_{HF} = (A' − A) = (B' − B) = (C' − C) = (D' − D) = 11 c.p.s.; J_{HF} = (D − C) = (B − A) = 171 c.p.s.

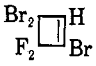
The cyclic Grignard reagent IIa was found to be unstable in excess ethylmagnesium bromide. On standing for 12 hr., this mixture gave, upon hydrolysis, three cyclobutenes in small yields. These were identified as 1-chloro-3,3-dibromo-4,4-difluorocyclobutene (VIII), 1,3-dibromo-3-chloro-4,4-difluorocyclobutene (IX), and 1,3,3-tribromo-4,4-difluorocyclobutene (X). A large amount of tar had also formed.



VIII



IX



X

The proton n.m.r. spectra triplet was centered at τ 3.10, 2.95, and 2.80, respectively. The spin–spin coupling (J_{HF} = 10 c.p.s.) indicates that the fluorines are across the ring from the proton.[8] The triplet observed for XI could not be resolved into two doublets which would be expected for two types of fluorines; however, F^{19} n.m.r. of IX shows two doublets, each peak of which is further split by a proton, proving that two types of fluorine exist (see Fig. 1). The relative intensities of the inner and outer lines is 3.26 to 1. F^{19} n.m.r. of VIII shows a single doublet with peaks at 5904 and 5925 c.p.s. and X also shows a doublet with peaks at 5812 and 5822 c.p.s. This is expected for a proton splitting a group of equivalent fluorines.

The infrared spectra of all three compounds are nearly identical, especially for isomers VIII and IX. Double bond absorption for IX and X is at 1560 and 1580 cm.$^{-1}$ for VIII. This is consistent with similar peaks for IIIa and b.

The structural assignments for VIII, IX, and X are further supported by mass spectral data. For VIII and IX, molecular ion peaks occur at m/e = 280, 282, 284, and 286 in the ratio expected for Br_2Cl (1.2% of Σ_{50} for VIII and 7.2% Σ_{50} for IX), and for X at m/e = 324, 326, 328, and 330. In each case the base peak corresponds to loss of bromine.

It was noted above that the reaction of ethylmagnesium bromide with IIIb and with 1-ethoxy-2-bromo-3,3,4,4-tetrafluorocyclobutene produced a rapid, mildly exothermic reaction that the only product was a mixture of high-boiling hydrocarbons. The high reactivity of the bromo ether was surprising, and it was thought that the vinylic ether group may be contributing to this reactivity.[9] For this reason the analogous chloro ether (XI) was treated with ethylmagnesium bromide in the hope that this compound would be less reactive

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[7] J. D. Park, J. Abromo, M. Hein, D. N. Gray, and J. R. Lacher, *J. Org. Chem.*, **23**, 1661 (1958).

[8] C. M. Sharts and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 1008 (1957).

[9] C. M. Hill, *et al.*, *ibid.*, **80**, 4602 (1958); **77**, 352 (1955).

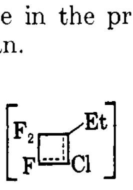
than the bromo ether and that some product or products would be isolated which would show some reaction of the ethoxy group with a Grignard reagent and also products which would show replacement of fluorine by ethyl groups.

Treatment of XI with ethylmagnesium bromide in tetrahydrofuran at 45° produced two major products identified as 1,2-diethyl-3,3,4,4-tetrafluorocyclobutene (XII) and 1-ethyl-2-chloro-3,3,4,4-tetrafluorocyclobutene (XIII), and three minor products. Two of the minor products, 1-chloro-2,3,3-trifluoro-4-ethyl-4-ethoxycyclobutene (XIV) and 1-chloro-2,3,3-trifluoro-4,4-diethylcyclobutene (XV), were examined using infrared and n.m.r. analysis. Molecular weights were determined using mass spectrographic analysis. Both compounds showed double bond absorption in the infrared at 1710–1720 cm.$^{-1}$, which indicates the presence of vinylic fluorine and chlorine. Methylene absorption in the n.m.r. spectrum of the allylic *gem*-diethoxy group in 1,3,3-ethoxy-2-bromo-4,4-difluorocyclobutene and for the analogous 2-iodo compound occurs at τ 6.2. The ethoxy methylene absorption in XIV occurs farther upfield, at τ 6.4, which would be expected since the ethoxy group in this case is geminal to an ethyl group and is more shielded. Methylene absorption for the allylic ethyl group in XIV occurs at τ 8.11, farther downfield than this methylene absorption in XV, which is at τ 8.35.

Neither compound contains a vinylic ethyl or ethoxy group since methylene absorption for these groups is at τ 7.8 and 5.5, as in compounds XIII and XI, respectively.

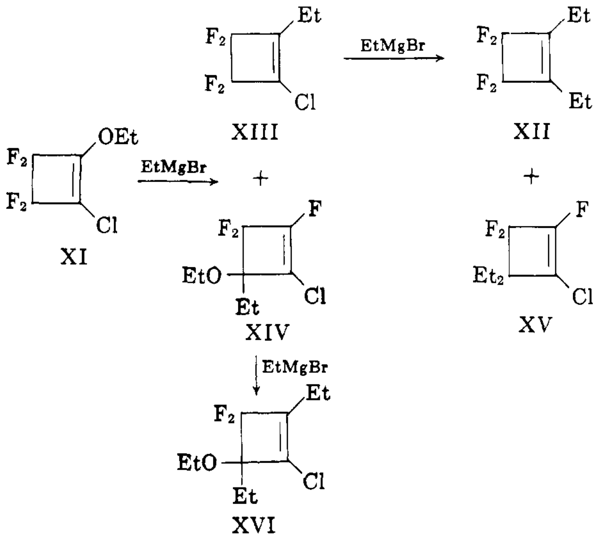
In order to determine the origin of the *gem*-diethyl compounds XV, the olefin XIII was prepared in an independent manner by reaction of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene and ethylmagnesium bromide and upon treatment with the same reagent yielded the 1,2-diethyl compound (XII), and XV was also isolated in minor amounts.

Formation of compounds XIV and XV are thought to demonstrate the operation of the S$_N$2′ reaction with a Grignard reagent. Formation of a mesomeric carbonium ion probably does not occur owing to the relatively high energy of such an ion. In addition, XIII was shown not to rearrange in the presence of magnesium salts in tetrahydrofuran.



The third minor product, 1,3-diethyl-2-chloro-3-ethoxy-4,4-difluorocyclobutene (XVI), was probably formed from XIV by replacement of vinylic fluorine by an ethyl group by reaction with ethylmagnesium bromide. The n.m.r. spectrum of XVI shows a multiplet at τ 6.4, due to methylene absorption of the allylic ethoxy group. A quartet appears at τ 7.8 due to vinylic methylene and an allylic methylene of the ethyl group appears at τ 8.3. Double bond absorption occurs at 1655 cm.$^{-1}$, which is the same as that for XIII.

On the basis of the above information, the reaction of XI with ethylmagnesium bromide is believed to proceed in the following way.



Experimental

Preparation of cyclobutanes by thermal cycloaddition reactions of the appropriate halogenated ethylenes were carried out following the general procedure outlined by Coffman, *et al.*[10] 1,1-Dichloro-3,3,4,4-tetrafluorocyclobutane was prepared by the codimerization of tetrafluoroethylene and vinylidene chloride by this method.

1-Chloro-3,3,4,4-tetrafluorocyclobutene (IIIa).—To a solution of 272 g. (2.7 moles) of triethylamine in 500 ml. of ether in a 2-l. three-neck flask fitted with reflux condenser, stirrer, and dropping funnel, and cooled in an ice bath was added dropwise 500 g. (2.5 moles) of 1,1-dichloro-3,3,4,4-tetrafluorocyclobutane. A white solid formed immediately. The mixture was stirred 2 hr. after addition was complete. Water was added to dissolve the triethylamine hydrochloride, the ether layer was washed with dilute hydrochloric acid, dried over anhydrous magnesium sulfate, and distilled to yield 325 g. (79% conversion) of IIIa, b.p. 53.4° (628 mm.), lit.[11] b.p. 53.8–54°. The n.m.r. spectrum showed a triplet at τ 3.45, J_{HF} = 10 c.p.s., which is consistent with a vinyl hydrogen split by two equivalent fluorines across the ring. Each peak of the triplet was further split into a triplet; the additional splitting ($J \approx 2$ c.p.s.) was due to two equivalent adjacent fluorines.[8]

1,2-Dibromo-1-chloro-3,3,4,4-tetrafluorocyclobutane.—To a gently stirred solution of 600 ml. of methylene chloride and 650 g. (4.05 moles) of IIIa, was added 744 g. (4.65 moles) of bromine. Gentle heating was provided by two 300-w. frosted light bulbs for 240 hr. The solution was then washed with sodium bisulfite, the low boilers were distilled off, and 1257.5 g. of crude product was obtained. A small sample of this adduct was distilled to yield 30 g. of the cyclobutane, b.p. 87.5° (126 mm.), n^{25}_{D} 1.4465, d^{25}_{25} 2.183, MR 39.29 (calcd., 39.74).

Anal. Calcd. for $C_4HBr_2ClF_4$: C, 14.99; H, 0.31; Br, 49.89; Cl, 11.06; F, 23.72. Found: C, 15.12; H, 0.52; Br, 49.91; Cl, 10.94; F, 23.68.

1-Bromo-2-chloro-3,3,4,4-tetrafluorocyclobutene (Ia).—To a solution of 180 g. (1.8 moles) of triethylamine in 300 ml. of ether and cooled in an ice bath was added dropwise 1248 g. (3.9 moles) of the crude 1,2-dibromo-1-chloro-3,3,4,4-tetrafluorocyclobutene. A white solid formed immediately. Stirring was continued overnight after addition was complete, and the product was retrieved as explained for IIIa above. Distillation of the ether layer yielded 553.7 g. (60% conversion) of Ia, b.p. 79.4° (626 mm.), d^{25}_{25} 1.836, n^{25}_{D} 1.3966, MR 31.37 (calcd., 31.51).

Anal. Calcd. for C_4BrClF_4: C, 20.06; Br, 33.38; Cl, 14.81; F, 31.74. Found: C, 19.92; Br, 33.46; Cl, 15.01; F, 31.80.

Also recovered was 36.8 g. (3.8% conversion) of 1,2-dibromo-3,3,4,4-tetrafluorocyclobutene (Ib), b.p. 95–96° (626 mm.), d^{25}_{25} 2.1147 (lit.[12] b.p. 92–94°, d^{25}_{25} 2.112). Small amounts of

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(10) D. D. Coffman, P. I. Barrick, R. D. Cramer, and M. S. Raasch, *J. Am. Chem. Soc.*, **71**, 490 (1949).

(11) J. D. Park, L. H. Wilson, and J. R. Lacher, *J. Org. Chem.*, **28**, 1008 (1963).

(12) R. V. Holler, Ph.D. Thesis, University of Colorado, 1957.

bromodichloromethane and bromoform were also isolated and identified by infrared analysis.

Reaction of Ia with Grignard Reagent.—To a solution of 60.2 g. (0.25 mole) of IV in 100 ml. of anhydrous ether and cooled in an ice bath was added dropwise 133 ml. of 3 *M* ethylmagnesium bromide (0.40 mole) at a rate such as to cause gentle reflux of the ether. The mixture was then stirred for 2 hr. and the Grignard reagent was destroyed by the addition of water. The mixture was extracted with ether and the ether extract was dried over anhydrous magnesium sulfate and distilled to yield 28.3 g. (71% conversion) of IIIa, b.p. 53.4° (628 mm.), n^{25}_{D} 1.3496. This product was formed by reaction of water with 2-chloro-3,3,4,4-tetrafluorocyclobutenylmagnesium bromide. This Grignard reagent is produced by an exchange reaction involving Ia and ethylmagnesium bromide.

This reaction was also carried out at 50° for 15 min. in tetrahydrofuran as a solvent, and also with methylmagnesium bromide in ether at 0°. In each case the same product, IIIa, was obtained, which was identified by its infrared spectrum.

1-Iodo-2-chloro-3,3,4,4-tetrafluorocyclobutene (IVa).—Exactly 80.7 g. (0.32 mole) of iodine was added over a period of 2 hr. to a solution of 2-chloro-3,3,4,4-tetrafluorocyclobutenylmagnesium bromide, prepared as described for above from 42.5 g. (0.18 mole) of Ia. The solution became very dark and a heavy precipitate formed. Stirring was continued 1 hr. after addition. The solution was then washed with a saturated solution of sodium bisulfite and the ether layer was dried over anhydrous magnesium sulfate. V.p.c. analysis (fluorosilicone column) of the ether extract revealed a 63% conversion to IVa. Distillation yielded 7.0 g. (22% yield) of IVa, b.p. 48° (70 mm.), n^{25}_{D} 1.4420, d^{25}_{25} 2.066, MR 36.55 (calcd., 36.70).

Anal. Calcd. for C_4IClF_4: I, 44.31. Found: I, 45.71.

Reaction of 1,2-Dibromo-3,3,4,4-tetrafluorocyclobutene with Grignard Reagent.—To a solution of 14.8 g. (0.052 mole) of the dibromide in 25 ml. of anhydrous ether was added 62 ml. of 3 *M* ethylmagnesium bromide (0.187 mole) in the manner described above for Ia. Separation of the product was effected on a preparative scale v.p.c. column (Dow Corning FS 1265 fluid) to yield 6.9 g. (65% conversion) of 1-bromo-3,3,4,4-tetrafluorocyclobutene (IIIb), b.p. 73.5° (624 mm.), n^{25}_{D} 1.3768 (lit.[13] b.p. 72-74°, n^{25}_{D} 1.3804), d^{25}_{25} 1.786, MR 26.39 (calcd., 26.64). The n.m.r. spectrum was similar to that for IIIa with the principal triplet centered at τ 3.05. This product was formed by reaction of water with the cyclic Grignard reagent which is produced by reaction of 1,2-dibromo-3,3,4,4-tetrafluorocyclobutene with ethylmagnesium bromide.

Anal. Calcd. for C_4HBrF_4: C, 23.63; H, 0.54; Br, 38.94; F, 36.85. Found: C, 23.43; H, 0.49; Br, 38.99; F, 37.08.

1-Iodo-2-bromo-3,3,4,4-tetrafluorocyclobutene (IVb).—To a solution of 2-chloro-3,3,4,4-tetrafluorocyclobutenylmagnesium bromide prepared from 14.2 g. (0.05 mole) of 1,2-dibromo-3,3,4,4-tetrafluorocyclobutene and 42 ml. of 3 *M* ethylmagnesium bromide (0.125 mole) and 25 ml. of anhydrous ether was added 31.7 g. (0.125 mole) of iodine. The solution remained a clear dark olive brown until all but a few grams of the iodine had been added. At this point the iodine colored the solution a deep violet, indicating completion of the reaction. Work-up was performed as described for the preparation of IVa above. Distillation yielded 9.6 g. (58.5% conversion) of IVb, b.p. 126.5° (614 mm.), d^{25}_{25} 2.3291, n^{25}_{D} 1.4671, MR 39.41 (calcd. 39.44).

Anal. Calcd. for C_4IBrF_4: C, 14.52; I, 38.31; Br, 24.15; F, 22.94. Found: C, 14.45; I, 38.13; Br, 23.90; F, 22.69.

Reaction of IVb with Ethylmagnesium Bromide.—To a solution of 2.5 g. (0.0075 mole) of IVb in 5 ml. of anhydrous ether contained in a 100-ml. three-neck flask was added dropwise 5.5 ml. (0.016 mole) of 3 *M* ethylmagnesium bromide. After an hour of stirring, the mixture was worked up as described for the preparation of IIIb above. The products were separated by preparative-scale v.p.c. (Dow Corning FS 1265 fluid) yielding 1-bromo-3,3,4,4-tetrafluorocyclobutene, and ethyl iodide which were identified by comparison of infrared spectra. No trace of any other products was noticed from v.p.c. analysis. When this reaction was carried out in tetrahydrofuran as a solvent, the same product was observed.

Reaction of IVb with ethylmagnesium bromide gives a cyclic Grignard reagent involving exchange of vinylic iodine. Reaction of this cyclic vinyl Grignard reagent with water gives the product observed.

Decomposition of 2-Chloro-3,3,4,4-tetrafluorocyclobutenylmagnesium Bromide.—The cyclic Grignard reagent was prepared as described above from 120 g. (0.5 mole) of Ia and 270 ml. (0.8 mole) of 3 *M* ethylmagnesium bromide and allowed to stand, with stirring, at room temperature for 12 hr. Water was then added and the very dark ether layer was dried and distilled to yield 10 g. (12.6% conversion) of IIIa, b.p. 53.4° (628 mm.), 14.7 g. (10.4% conversion) of a mixture of isomers 1-chloro-3,3-dibromo-4,4-difluorocyclobutene (VIII), b.p. 157° (613 mm.), and 1,3-dibromo-3-chloro-4,4-difluorocyclobutene (IX), b.p. 156° (623 mm.), which were separated in a 20-ft. preparative-scale tricresyl phosphate (TCP) column at 100°. The mixture of isomers consisted of 46% of VIII, d^{25}_{25} 2.03, and 54% of IX, d^{25}_{25} 2.114, n^{25}_{D} 1.5091; MR of IX; 39.88 (calcd., 39.08). Elemental analysis of the mixture was the same as that for IX alone. Also isolated by preparative-scale v.p.c. (Dow Corning FS 1265 fluid) was 1.5 g. (0.46% conversion) of 1,3,3-tribromo-4,4-difluorocyclobutene (X) b.p. 179° (613 mm.), n^{25}_{D} 1.5408, d^{25}_{25} 2.44. The bulk of the material was present as tar.

Anal. Calcd. for $C_4HBr_2ClF_2$: C, 17.02; H, 0.35; Br, 56.60; Cl, 12.59; F, 13.46. Found: C, 17.09; H, 0.40; Br, 56.55; Cl, 12.45; F, 13.50.

Anal. Calcd. for $C_4HBr_3F_2$: C, 14.70; H, 0.39; Br, 73.36; F, 11.63. Found: C, 15.22; H, 0.46; Br, 73.85; F, 11.61.

Reaction of 1-Ethoxy-2-bromo-3,3,4,4-tetrafluorocyclobutene with Grignard Reagent.—To a solution of 19.2 g. (0.077 mole) of XI in anhydrous ether and cooled in an ice bath was added dropwise 107 ml. of 3 *M* *n*-butylmagnesium chloride (0.3 mole). A gentle exothermic reaction ensued. The reaction mixture was stirred for 3 hr. and worked up as before. The ether layer was distilled to yield *n*-butyl bromide, which was identified by comparison of its infrared spectrum with that of an authentic sample; a small amount of the starting bromo ether and a high-boiling mixture of hydrocarbons, boiling range 106–138° (2 mm.). A higher boiling residue was also obtained. Infrared analysis of the distilled portions and of the pot residue revealed strong bands in the 2850–2960-cm.$^{-1}$ region and medium bands at 1370 and 1450–1465 cm.$^{-1}$ and weak absorption in the 1000–1400-cm.$^{-1}$ range which may be due to C–F stretching.

Reaction of 1-Bromo-3,3,4,4-tetrafluorocyclobutene (IIIb) with Grignard Reagent.—To a solution of 0.17 g. (0.00083 mole) of IIIb in 2 ml. of tetrahydrofuran was added 5.5 ml. (0.0016 mole) of 3 *M* ethylmagnesium bromide. The solution was warmed to 55° on a steam bath for 2 hr. The mixture was worked up as described above and distilled to yield ethyl bromide and a high-boiling hydrocarbon residue similar to that of the bromo ether above and with weak C–F absorption in the range 1000–1400 cm.$^{-1}$.

1,1-Difluoro-1,2,2-tribromoethane.—This compound of b.p. 124–125° (621 mm.), n^{25}_{D} 1.4971 (Holler[12] reports n^{25}_{D} 1.4974), was obtained in quantitative yield after the manner of Holler[12] by bubbling gaseous 1,1-difluoro-2-bromoethylene through liquid bromine at atmospheric pressure. The 1,1-difluoro-2-bromoethylene, b.p. 3° (625 mm.), was obtained according to the procedure of Gray[6] in 70% yield by first bubbling 1,1-difluoroethylene through bromine under ultraviolet irradiation to produce the dibromide in quantitative yield which was then treated with a heated suspension of potassium hydroxide in mineral oil.

1,1-Difluoro-2,2-dibromoethylene.—To a solution of 1212 g. (4 moles) of the tribromide in 400 ml. of ether in a 2-l. three-neck flask was added 430 g. (4.3 moles) of triethylamine. The solution was stirred and warmed gently for 5 hr. A white precipitate formed which was dissolved in water. The ether solution was washed with dilute hydrochloric acid, dried over anhydrous magnesium sulfate, and distilled to yield 723 g. (91.2% conversion) of 1,1-difluoro-2,2-dibromoethylene, b.p. 62–63° at 621 mm., n^{25}_{D} 1.4421 (lit.[12] b.p. 63° at 634 mm., n^{25}_{D} 1.4423). Also recovered was 86 g. of the starting tribromide.

1,1-Dibromo-2-chloro-2,3,3,4,4-pentafluorocyclobutane.—A 1.5-l. stainless steel Paar bomb was charged with 156 g. (1.34 moles) of chlorotrifluoroethylene and 149 g. (0.67 mole) of 1,1-difluoro-2,2-dibromoethylene and 1 ml. of *d*-limonene inhibitor. The bomb was shaken and heated to 175° over a period of 24 hr. and then maintained at this temperature for 24 hr. The gaseous products were bled from the bomb and the liquid product was distilled to give, as the major product, a semisolid material which was purified by crystallization from a methanol–water mixture to give 41 g. (18% conversion) of a colorless solid, m.p. 52–54°,

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[13] I. L. Knunyants, M. P. Krasuskays, E. I. Mysov, and I. A. Mukhtarov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2141 (1962); *Chem. Abstr.*, **55**, 19775*g* (1963).

b.p. 126–126.5° (623 mm.). The solid has a high vapor pressure and a camphor-like odor.

Anal. Calcd. for $C_4Br_2ClF_5$: C, 14.20; Br, 47.24; Cl, 10.47; F, 28.08. Found: C, 14.15; Br, 47.45; Cl, 10.43; F, 28.29.

1-Bromo-2,3,3,4,4-pentafluorocyclobutene (V).—A solution of 8.8 g. (0.026 mole) of the above cyclobutane in ethanol was added to a warm slurry of zinc in ethanol. A vigorous reaction ensued to yield 5 g. (85% conversion) of V, b.p. 48° (626 mm.), d^{25}_{25} 1.799, $n^{25}\mathrm{D}$ 1.3494, MR 26.62 (calcd., 26.74).

Anal. Calcd. for C_4BrF_5: C, 21.54; Br, 35.84; F, 42.61. Found: C, 21.68; Br, 35.48; F, 42.63.

Reaction of V with Ethylmagnesium Bromide.—To a solution of 4.9 g. (0.022 mole) of V in 10 ml. of anhydrous ether and cooled to 0°, was added rapidly 15 ml. (0.045 mole) of 3 *M* ethylmagnesium bromide. After stirring 1 hr., water was added, the ether solution was dried, and the products were separated by preparative-scale v.p.c. to yield 0.92 g. (30% recovery) of 2,3,3,4,4-pentafluorocyclobutene (VI) and 0.55 g. (23% recovery) of ethyl bromide. These compounds were identified by their infrared spectra. Also isolated was 0.06 g. (0.9% recovery) of 1-ethyl-2-bromo-3,3,4,4-tetrafluorocyclobutene (VII). The infrared spectrum of this compound was nearly identical with that for the 2-chloro analog (XIII). The low yields are attributable to poor recovery from the chromatograph. No other products were observed.

Anal. Calcd. for $C_6H_5BrF_4$: C, 30.92; H, 2.16; Br, 34.30; F, 32.62. Found: C, 30.95; H, 2.10; Br, 34.15; F, 32.81.

Reaction of 1-Ethoxy-2-chloro-3,3,4,4-tetrafluorocyclobutene (XI) with Ethylmagnesium Bromide.—A solution of 123.8 g. (0.60 mole) of XVII in 300 ml. of anhydrous tetrahydrofuran in a 1-l. three-neck flask was stirred and warmed to 50°. To this was added dropwise 400 ml. (1.2 moles) of ethylmagnesium bromide in ether. The ether was distilled during addition. After stirring for 4 hr., a heavy precipitate formed, and the reaction had to be discontinued. Water was added to dissolve the solid and the product was taken up in ether and dried over magnesium sulfate. Distillation yielded 12 g. (15.3% conversion) of 1-ethyl-2-chloro-3,3,4,4-tetrafluorocyclobutene (XIII), b.p. 98–99° (620 mm.), $n^{25}\mathrm{D}$ 1.3709. This was identified by comparison of the infrared spectrum with that of an authentic sample. Also recovered by distillation was a mixture of 1,2-diethyl-3,3,4,4-tetrafluorocyclobutene (XII), 1-chloro-2,3,3-trifluoro-4,4-diethylcyclobutene (XV), 1-chloro-2,3,3-trifluoro-4-ethyl-4-ethoxycyclobutene (XIV), and starting material (XI). Separation of XII was effected in 16.6% conversion using a fluorosilicone preparative-scale v.p.c. column (12.6 g., b.p. 134–136° at 620 mm.). Also separated in this manner was 40 g. of XI and a mixture of XIV and XV. This mixture was resolved by use of a tricresyl phosphate column to give 3.4 g. of XV (4.2% conversion), b.p. 133° (619 mm.), d^{25}_{25} 1.159, $n^{25}\mathrm{D}$ 1.4018, MR 41.91 (calcd., 42.12), and 4.2 g. of XIV (5% conversion), b.p. 136–137° (619 mm.), d^{25}_{25} 1.185, $n^{25}\mathrm{D}$ 1.3979, MR 43.68 (calcd. 43.76).

Anal. Calcd. for $C_8H_{10}F_3Cl$ (XV): C, 48.37; H, 5.07; Cl, 17.85; F, 28.70. Found: C, 48.33; H, 5.17; Cl, 17.86; F, 28.82.

Anal. Calcd. for $C_8H_{10}F_3ClO$ (XIV): C, 44.76; H, 4.70; Cl, 16.52; F, 26.56. Found: C, 44.82; H, 4.80; Cl, 16.71; F, 26.77.

Also isolated was 1.5 g. (1.8% conversion) of 1-chloro-2,4-diethyl-3,3-difluoro-4-ethoxycyclobutene (XVI), b.p. 175° (619 mm.) (with some decomposition), d^{25}_{25} 1.081, $n^{25}\mathrm{D}$ 1.4238, MR 53.00 (calcd. 52.90). The compound turns yellow after several weeks at room temperature.

Anal. Calcd. for $C_{10}H_{15}ClF_2O$: C, 53.45; H, 6.73; Cl, 15.78; F, 16.92. Found: C, 54.47; H, 7.09; Cl, 15.85; F, 17.18.

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Derivatives of 1,2,3,4-Tetramethylcyclobutene. Interconversion of Cations in Sulfuric Acid[1]

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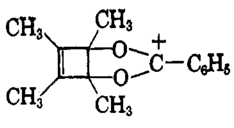
Semiquantitative data on the equilibria between the stable bridged cations derived from 1,2,3,4-tetramethylcyclobutene-1,2-diol benzoates are presented. The mechanism of exchange is discussed.

In a previous paper[3] it has been reported that in 97% sulfuric acid benzoate esters of 1,2,3,4-tetramethylcyclobutene-1,2-diol form the stable bridged cation I. Two properties of this cation are interesting. On the one hand an n.m.r. spectrum of I indicates that an intramolecular rearrangement occurs with sufficient rapidity so as to coalesce the two methyl bands into a single sharp peak.[4] At the same time addition of *p*-nitrobenzoic acid to sulfuric acid solutions of I lead to rapid and reversible intermolecular exchange of the benzoate fragments to provide the *p*-nitro-substituted cation analogous to I. This paper will present additional semiquantitative data on the intermolecular exchange process. The possible mechanisms and energy barriers for the intramolecular and intermolecular exchanges will be considered.



I

Results

The observation[3] of facile exchange of benzoate by *p*-nitrobenzoate in the bridged cation prompted the determination of the effect of substituents on the equilibrium constants for the exchange reaction shown in eq. 1. The equilibrium constant (eq. 2) has been defined in terms of protonated benzoic acid species since this is the predominant form of the acids in the 96–97% sulfuric acid used as the solvent.[5]

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[1] Taken from the dissertation submitted by D. L. Nealy in partial fulfillment of the requirements for the Ph.D. degree, Cornell University, June, 1963.

[2] National Science Foundation Predoctoral Fellow, 1959–1963.

[3] C. F. Wilcox, Jr., and D. L. Nealy, *J. Org. Chem.*, **28**, 3446 (1963).

[4] Evidence to be presented in this paper indicates that this peak does not arise from a fortuitous overlapping of the separate methyl bands.

[5] R. Stewart and M. R. Granger, *Can. J. Chem.*, **39**, 2508 (1961); R. Stewart and K. Yates, *J. Am. Chem. Soc.*, **82**, 4059 (1960).