

London, for the use of their polarimeter and other laboratory facilities for the kinetic measurements. Finally, the author wishes to sincerely thank Martin Grossel at King's College for so generously sharing his limited laboratory and fumehood space, glassware,

solvents, and routine laboratory chemicals and apparatus with a visitor from the "colonies."

Registry No.—(+)-1-Phenylbromoethane, 1459-14-9; (−)-1-phenylbromoethane, 3756-40-9.

## Methyl-Substituted Fluorine-Containing Cyclobutenes. Establishment of the HF Coupling Constants between a Vinylic Methyl Group and the Ring Fluorines<sup>1a</sup>

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Halogen interchange reactions with aluminum chloride on 1,2-dimethyl-3,3,4,4-tetrafluorocyclobutene and 1-methyl-2,3,3,4,4-pentafluorocyclobutene have been shown to lead to 1,2-dimethyl-3,3-difluoro-4,4-dichlorocyclobutene (2) and 1-methyl-3,3-difluoro-2,4,4-trichlorocyclobutene (5), respectively. The assignment of the HF coupling constants between the vinylic methyl group and the allylic ring fluorines in the nmr spectra for these materials was aided by compounds produced by alternate synthetic pathways. Thus, 1-methyl-1,2,2-trichloro-3,3-difluorocyclobutene (7), prepared by a thermal codimerization technique, served as the starting material for the synthesis of 1-methyl-2-chloro-3,3-difluorocyclobutene (8) and 1-methyl-3,3-difluoro-4,4-dichlorocyclobutene (9).

Fluorocyclobutenes are known to undergo a facile substitution of the vinylic halide with methyl lithium<sup>2a-c</sup> and methyl Grignard reagents<sup>2d</sup> to yield monomethyl- or dimethylperfluorocyclobutenes. Studies on the chemical reactivity of these materials have been concerned with hydrolysis of the ring fluorines,<sup>2c</sup> the halogenation of the vinylic methyl group,<sup>2b</sup> and elimination reactions which occur in the presence of alkoxide ions.<sup>3</sup> This paper reports on a halogen interchange reaction with aluminum chloride to produce methyl-substituted fluorochlorocyclobutenes and chlorocyclobutenes and the assignment of the HF coupling constants between the vinylic methyl group and the allylic ring fluorines in the nmr spectra.

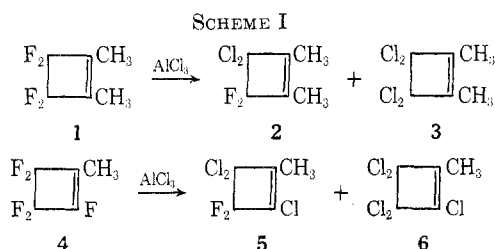
Halogen interchange with aluminum halides has been observed to take place with fluorinated cyclobutenes with particular ease.<sup>4</sup> Application of this convenient technique to 1,2-dimethyl-3,3,4,4-tetrafluorocyclobutene led to the characterization of two major products, 1,2-dimethyl-3,3-difluoro-4,4-dichlorocyclobutene (2) and 1,2-dimethyl-3,3,4,4-tetrachlorocyclobutene (3), as indicated in Scheme I. The proton nmr spectrum of 2

consisted of a triplet at  $\tau$  8.29 with a coupling constant  $J = 1.6$  Hz and a triplet at  $\tau$  8.17,  $J = 3.2$  Hz, as indicated in Table I along with the nmr data obtained

TABLE I  
NMR SPECTRA FOR CYCLOBUTENES

Compd	$\phi^*$	$\tau$	Group	Coupling
$\text{Cl}_2 \square \text{CH}_3$ $\text{F}_2 \square \text{CH}_3$		8.29	$\text{CH}_3$	t, $J = 1.6$ Hz
		8.17	$\text{CH}_3$	t, $J = 3.2$ Hz
$\text{Cl}_2 \square \text{CH}_3$ $\text{F}_2 \square \text{Cl}$	110.4	8.03	$\text{CH}_3$	t, $J = 3.1$ Hz
			Ring $\text{CF}_2$	q, $J = 3.1$ Hz
$\text{Cl}_2 \square \text{CH}_3$ $\text{F}_2 \square \text{H}$		7.99	$\text{CH}_3$	d, t, $J = 1.5$ , 3.2 Hz
		4.04	Vinyl H	m, $J = 1.5$ , 2.2 Hz
$\text{H}_2 \square \text{CH}_3$ $\text{F}_2 \square \text{Cl}$		104.6	Ring $\text{CF}_2$	d, q, $J = 2.2$ , 3.2 Hz
		8.09	$\text{CH}_3$	t, t, $J = 3.3$ , 1.3 Hz
$\text{H}_2 \square \text{Cl}^a$ $\text{F}_2 \square \text{CH}_3$		7.15	Ring $\text{CH}_2$	t, q, $J = 2.7$ , 1.3 Hz
		111.3	Ring $\text{CF}_2$	t, q, $J = 2.7$ , 3.3 Hz
$\text{H}_2 \square \text{Cl}^a$ $\text{F}_2 \square \text{CH}_3$		8.29	$\text{CH}_3$	t, t, $J = 1.6$ , 2.3 Hz
		6.92	Ring $\text{CH}_2$	t, q, $J = 2.7$ , 2.3 Hz
		112.5	Ring $\text{CF}_2$	t, q, $J = 2.7$ , 1.6 Hz

<sup>a</sup> Data obtained from ref 8. Compound prepared from  $\text{CH}_3\text{Li}$  and 1-chloro-2,3,3-trifluorocyclobutene.



(1) (a) Taken in part from the Ph.D. dissertation of T. S. Croft, University of Colorado, 1967. (b) To whom inquiries should be sent. Address correspondence to Central Research Laboratories, 3M Co., St. Paul, Minn. 55133.

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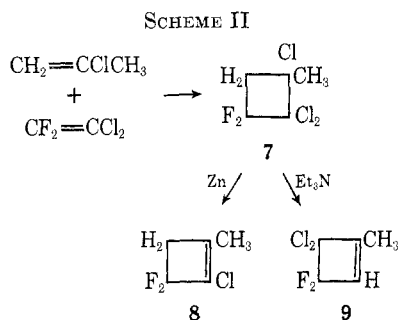
for all of the methyl-substituted fluorocyclobutenes discussed in this report. Since the cross ring allylic fluorines would be expected to deshield the vinylic methyl protons more than do adjacent fluorines,<sup>5</sup> this resonance should occur at a lower field position and the coupling constant for the vinylic methyl protons coupled with cross ring allylic fluorines must be 3.2 Hz, thus

(5) (a) Unpublished results, this laboratory: J. H. Adams, Ph.D. Dissertation, University of Colorado, 1965; (b) J. D. Park, J. R. Dick, and J. H. Adams, *J. Org. Chem.*, **30**, 400 (1965); (c) J. D. Park, G. Groppelli, and J. H. Adams, *Tetrahedron Lett.*, 103 (1967).

larger than the value of 1.6 Hz for adjacent allylic fluorines. This would be consistent with the data of Sharts and Roberts,<sup>6</sup> who reported that the HF coupling constant of a vinylic proton with the cross ring fluorines, through four bonds, was larger than that found with vicinal fluorines, through three bonds.

Scheme I also depicts the products, compounds 5 and 6, obtained from aluminum chloride and 1-methyl-2,3,3,4,4-pentafluorocyclobutene (4), the assignment of the structure of 5 as 1-methyl-3,3-difluoro-2,4,4-trichlorocyclobutene being based upon the coupling constant of 3.1 Hz observed in the nmr spectrum.

To establish definitively the coupling constant of the vinylic methyl group with the cross ring allylic fluorines, the synthesis of 1-methyl-2-chloro-3,3-difluorocyclobutene (8) and 1-methyl-3,3-difluoro-4,4-dichlorocyclobutene (9) was carried out as shown in Scheme II.



The thermal codimerization of 1,1-dichloro-2,2-difluoroethylene and 2-chloropropene would be predicted<sup>7</sup> to produce 1-methyl-1,2,2-trichloro-3,3-difluorocyclobutane (7), an assignment borne out by the nmr and mass spectra reported in the Experimental Section. Dechlorination of 7 with zinc gave 8 and a dehydrohalogenation induced with triethylamine produced 9. In both cases, the nmr spectra contained a coupling value of about 3.2 Hz from the cross ring allylic fluorines and the vinylic methyl protons. The magnitude of the coupling value of fluorines  $\beta$  to the vinylic methyl group in 1-chloro-2-methyl-3,3-difluorocyclobutene, an isomer of 8, was 1.6 Hz.<sup>8</sup> These data provide convincing evidence for the coupling and structural assignments.

### Experimental Section

Infrared spectra were taken on a Perkin-Elmer Infracord spectrophotometer. The nuclear magnetic resonance spectra were obtained from a Varian XL-100 spectrometer, utilizing an internal standard of  $\text{CFCl}_3$  for the determination of  $^{19}\text{F}$  chemical shifts, reported as  $\phi^*$  values,<sup>9</sup> and tetramethylsilane as reference<sup>10</sup> for the proton values. Product analyses and preparative scale separations were carried out on an Aerograph Autoprep Model A-700 utilizing a column with a fluorosilicone 1265 (QF-1) substrate. A Bausch and Lomb refractometer was used to measure the refractive indices. Densities were determined by weight difference with a calibrated 10- $\mu\text{l}$  syringe. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. The mass spectrum was taken on a CEC 21 110c mass spectrometer.

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**1-Methyl-2,3,3,4,4-pentafluorocyclobutene (4).**—The title compound was prepared following the procedure of Park and Fontanelli,<sup>2a</sup> bp 46–47° (626 mm) [lit.<sup>2a</sup> bp 44–45° (630 mm)].

**1,2-Dimethyl-3,3,4,4-tetrafluorocyclobutene (1).**—The procedure of Dixon<sup>2a</sup> was used to prepare the desired compound: bp 98–98.5° (626 mm);  $n_D^{25}$  1.3475 [lit.<sup>2a</sup> bp 100–104° (760 mm);  $n_D^{25}$  1.3478].

**Reaction of 1,2-Dimethyl-3,3,4,4-tetrafluorocyclobutene (1) with Aluminum Chloride.**—To an ice-cooled mixture of 11 g of aluminum chloride (B and A reagent powder) and 40 ml of carbon disulfide, under nitrogen atmosphere, was added 21 g of 1,2-dimethyl-3,3,4,4-tetrafluorocyclobutene. After stirring at room temperature for 16 hr, water was added, the black solution was filtered, and the organic layer was dried with anhydrous magnesium sulfate. Distillation gave 10 g of 1,2-dimethyl-3,3-dichloro-4,4-difluorocyclobutene (2): bp 139° (629 mm);  $n_D^{25}$  1.4334;  $d_4^{25}$  1.27; molar refractivity, calcd 37.7, found 37.4; ir 1680  $\text{cm}^{-1}$  ( $\text{CH}_3\text{C}=\text{CCH}_3$ ).

*Anal.* Calcd for  $\text{C}_6\text{H}_8\text{Cl}_2\text{F}_2$ : C, 38.50; H, 3.21; Cl, 37.97; F, 20.32. Found: C, 38.57; H, 3.13; Cl, 38.13; F, 20.25.

Also isolated was 2 g of 1,2-dimethyl-3,3,4,4-tetrachlorocyclobutene (3): bp 201.5–202.5° (629 mm);  $n_D^{25}$  1.5037;  $d_4^{25}$  1.40; molar refractivity, calcd 47.2, found 46.2; ir 1630  $\text{cm}^{-1}$  ( $\text{CH}_3\text{C}=\text{CCH}_3$ ); nmr ( $\text{CCl}_4$ )  $\tau$  8.12 (s,  $\text{CH}_3$ ).

*Anal.* Calcd for  $\text{C}_6\text{H}_8\text{Cl}_4$ : C, 32.73; H, 2.73; Cl, 64.54. Found: C, 32.94; H, 2.73; Cl, 64.49.

Traces of other products were noted by glc but were not isolated in sufficient quantities to be characterized.

**Reaction of 1-Methyl-2,3,3,4,4-pentafluorocyclobutene (4) with Aluminum Chloride.**—The dropwise addition of 25 g of 1-methyl-2,3,3,4,4-pentafluorocyclobutene to a suspension of 23 g of aluminum chloride in 75 ml of carbon disulfide cooled in ice turned the solution black. After 5 hr under a nitrogen flow, the mixture was filtered, the solid being extracted with methylene chloride. The organic layer was dried and distilled to give 10 g of 1-methyl-2,4,4-trichloro-3,3-difluorocyclobutene (5): bp 139–139.5° (632 mm);  $n_D^{25}$  1.4489;  $d_4^{25}$  1.50; molar refractivity, calcd 37.82, found 37.35; ir 1670  $\text{cm}^{-1}$  ( $\text{ClC}=\text{CCH}_3$ ).

*Anal.* Calcd for  $\text{C}_5\text{H}_7\text{Cl}_3\text{F}_2$ : C, 28.89; H, 1.45; Cl, 51.30; F, 18.32. Found: C, 29.19; H, 1.65; Cl, 50.94; F, 18.38.

A trace was also found of 1-methyl-2,3,3,4,4-pentachlorocyclobutene (6): mp 50.5–52.5; bp 203–203.5° (627 mm); ir 1670  $\text{cm}^{-1}$  ( $\text{ClC}=\text{CCH}_3$ ); nmr ( $\text{CCl}_4$ )  $\tau$  8.03 (s,  $\text{CH}_3$ ).

*Anal.* Calcd for  $\text{C}_5\text{H}_7\text{Cl}_5$ : C, 24.95; H, 1.25; Cl, 73.84. Found: C, 25.16; H, 1.32; Cl, 73.74.

Traces of other products were also seen in the glc curve of the product but were not characterized.

**Codimerization of 2-Chloropropene and 1,1-Dichloro-2,2-difluoroethylene.**—In a 0.5-l. autoclave, 76 g of 2-chloropropene and 132 g of 1,1-dichloro-2,2-difluoroethylene, along with 1 ml of *d*-limonene to prevent polymerization, were heated to 180° for 12 hr. Distillation of the yellow liquid gave 7 g of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene, bp 60.5° (628 mm), and 30 g of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane, bp 124° (628 mm), both identified by comparison with the infrared spectra of authentic samples.<sup>11</sup> Also collected was 31 g of 1-methyl-1,2,2-trichloro-3,3-difluorocyclobutane (7): mp 46–49°; bp 148° (628 mm); nmr ( $\text{CFCl}_3$ )  $\tau$  8.09 (d,  $J = 1.2$  Hz,  $\text{CH}_3$ ), 6.93 and 7.11 (AB pattern,  $J_{AB} = 13.8$  Hz, ring  $\text{CH}_2$ ), with fine structure visible, with 6.93 (d, d,  $J = 9.5, 15.2$  Hz, ring CH) and 7.11 (d, d,  $J = 11.8, 6.5$  Hz, ring CH),  $\phi^* 98.10$  and 102.31 (AB pattern,  $J_{AB} = 190.0$  Hz,  $\text{CF}_2$ ) with fine structure visible, with 98.10 (d, d,  $J = 9.5, 6.4$  Hz, CF) and 102.31 (d, d, q,  $J = 11.6, 15.1, 1.2$  Hz, CF); mass spectrum ( $150^\circ$   $m/e$  (ion) in decreasing order of intensity, 76 ( $\text{CH}_2\text{CClCH}_3$ ), 144 (P –  $\text{CF}_2\text{CH}_2$ ), 109 (P –  $\text{CH}_2\text{CF}_2$ , Cl), 41 ( $\text{C}_3\text{H}_5$ ), 39 ( $\text{C}_2\text{H}_3$ ), 132 ( $\text{CF}_2\text{CCl}_2$ ), 51 ( $\text{CF}_2\text{H}$ ), 64 ( $\text{CF}_2\text{CH}_2$ ), 172 (P – HCl), 208 (P).

*Anal.* Calcd for  $\text{C}_5\text{H}_7\text{Cl}_3\text{F}_2$ : C, 28.64; H, 2.39; Cl, 50.08; F, 18.14. Found: C, 28.87; H, 2.50; Cl, 50.71; F, 18.36.

**Reaction of 1-Methyl-1,2,2-trichloro-3,3-difluorocyclobutane (7) with Zinc.**—After a mixture of 10 g of 1-methyl-1,2,2-trichloro-3,3-difluorocyclobutane, 0.5 ml of hydrochloric acid, and 6.5 g of zinc was heated in 1-butanol for 24 hr, distillation gave 4 g of 1-methyl-2-chloro-3,3-difluorocyclobutene (8): bp 100° (633 mm);  $n_D^{25}$  1.3998;  $d_4^{25}$  1.18; molar refractivity, calcd 28.2, found 28.2; ir 1670  $\text{cm}^{-1}$  ( $\text{ClC}=\text{CCH}_3$ ).

*Anal.* Calcd for  $\text{C}_5\text{H}_7\text{ClF}_2$ : C, 43.32; H, 3.61; Cl, 25.63; F, 27.80. Found: C, 43.41; H, 3.70; Cl, 25.80; F, 27.39.

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**Reaction of 1-Methyl-1,2,2-trichloro-3,3-difluorobutane (7) with Triethylamine.**—A 10-g sample of 1-methyl-1,2,2-trichloro-3,3-difluorocyclobutane was refluxed with 7.5 g of triethylamine for 91 hr. After washing with hydrochloric acid, separation, and drying, 4 g of starting material was recovered by distillation. Also isolated was 4 g of 1-methyl-3,3-difluoro-4,4-dichlorocyclobutene (9): bp 130° (629 mm);  $n_D^{25}$  1.4261;  $d_4^{25}$  1.34; molar refractivity, calcd 33.0, found, 32.9;  $\nu$  1645  $\text{cm}^{-1}$  ( $\text{HC}=\text{CCH}_3$ ).

*Anal.* Calcd for  $\text{C}_5\text{H}_4\text{Cl}_2\text{F}_2$ : C, 34.68; H, 2.31; Cl, 41.04; F, 21.96. Found: C, 34.79; H, 2.38; Cl, 41.09; F, 21.83.

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Sparrow of the 3M Co., St. Paul, Minn., for having run the  $^{19}\text{F}$  nmr spectra and the mass spectrum reported in this paper. We also wish to thank AFOSR Chemical Division and the 3M Co., St. Paul, Minn., for their support of this work.

**Registry No.**—1, 356-58-1; 2, 41785-17-5; 3, 41785-18-6; 4, 356-59-2; 5, 41785-19-7; 6, 41785-20-0; 7, 41785-21-1; 8, 41785-22-2; 9, 41785-23-3; aluminum chloride, 7446-70-0; 2-chloropropene, 557-98-2; 1,1-dichloro-2,2-difluoroethylene, 79-35-6; 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene, 377-93-5; 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane, 336-50-5; zinc, 7740-66-6; triethylamine, 121-44-8.

## Fluorinated Esters Stable to Fluoride Ion

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Some new fluorinated esters,  $\text{CF}_3\text{CO}_2\text{R}_f$  [ $\text{R}_f = (\text{CF}_3)_3\text{C}$ ,  $\text{C}_2\text{F}_5(\text{CF}_3)_2\text{C}$ ,  $(\text{CF}_3)_2(\text{CH}_3)\text{C}$ , and  $(\text{CF}_3)_2\text{CH}$ ], with substituents other than fluorine on the alkoxy  $\alpha$  carbon have been prepared using the cesium fluoride catalyzed reactions of trifluoroacetyl fluoride with fluoro alcohols. Unlike the fluorinated esters with fluorine at the alkoxy  $\alpha$  carbon atom, these esters are stable in the presence of fluoride ion at 25° or higher temperatures. Their ir, nmr, and mass spectra are reported.

In our earlier studies,<sup>1</sup> we had observed that, while the totally fluorinated esters were stable at 25° and above when pure, they disproportionated readily at  $>-78^\circ$  in the presence of fluoride ions. Each of these esters contained a perfluoroalkoxy group with at least one fluorine atom bonded to the  $\alpha$  carbon adjacent to the oxygen,  $-\text{OCR}_f(\text{R}'_f)\text{F}$  ( $\text{R}_f = \text{CF}_3$ ,  $\text{R}'_f = \text{F}$ ;  $\text{R}_f = \text{R}'_f = \text{CF}_3$ ). We now have extended our study to a variety of other esters with different substituents on that carbon to determine their stabilities to attack by fluoride ions.

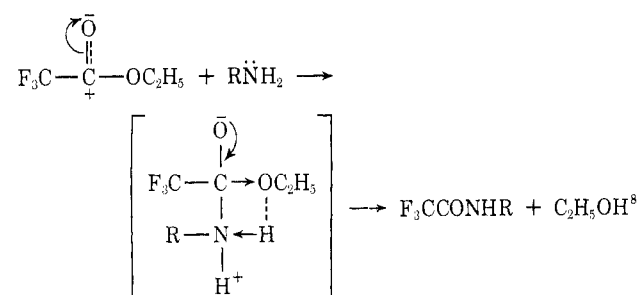
Contrary to the well-known reactions of acid chlorides with alcohols, the corresponding reactions of acid fluorides have neither been as popular nor as lucrative; e.g., trifluoroacetyl fluoride with ethanol yielded a trace of ethyl trifluoroacetate,  $\text{CF}_3\text{CO}_2\text{C}_2\text{H}_5$ , accompanied by other products.<sup>2</sup> However, we found that a modification of this route provided a good general preparative method for esters.

Although some of the esters described in this paper have been previously reported,<sup>3-7</sup> little spectral characterization was included. Full details of infrared, mass, and  $^1\text{H}$  and  $^{19}\text{F}$  nmr spectra are given.

### Results and Discussion

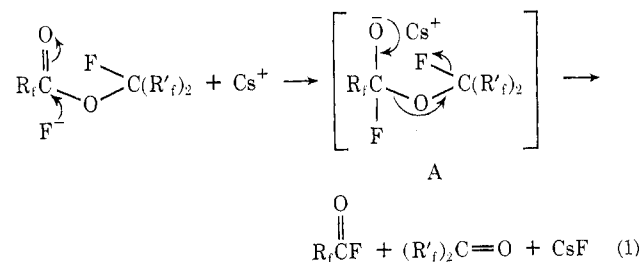
Fluorinated esters of the type  $\text{R}_f\text{CO}_2\text{CF}(\text{CF}_3)_2$  which contain fluorine on the alkoxy  $\alpha$  carbon are unstable in the presence of fluoride ion at  $-78^\circ$  or above.<sup>1</sup> However, esters described in this paper that contain substituents other than fluorine at this carbon are very

stable in the presence of fluoride ion even at higher temperatures. Since  $\text{R}_f$  is an electronegative group, it enhances the electrophilic character of the carbonyl carbon atom and thus promotes addition to the carbonyl double bond.



The fluoride ion, which is strongly nucleophilic, can readily attack at the positive carbon of the carbonyl group to form a similar intermediate which will then disproportionate to give the acid fluoride.

Owing to the very strong inductive effect of F, its departure as shown in eq 1 will be favored. However,



the inductive effects of  $\text{CF}_3$  and particularly of H and  $\text{CH}_3$  are very much less than that of fluorine.<sup>8b</sup> Thus, these moieties will not be good leaving groups in a complex like A. This explains the greater stability of the

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