

Synthesis and Properties of Some Fluorinated Ketones¹

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Ketones containing one perfluoroalkyl group have been prepared² by the reactions of perfluorinated acids with Grignard reagents. In this study, a variety of ketones of the type $\text{Cl}(\text{CF}_2-\text{CFCl})_n-\text{CF}_2-\text{CO}-\text{R}$ where $n=1, 2,$ and 3 and $\text{R}=\text{methyl}$ and ethyl groups were prepared by the action of RMgBr on $\text{Cl}(\text{CF}_2\text{CFCl})_n\text{CF}_2\text{COOH}$. Ketones of the type $\text{R}_F-\text{CO}-\text{R}$, where $\text{R}_F = -\text{CF}_3$ and $-\text{C}_2\text{F}_5$ and $\text{R} = \text{methyl, ethyl, and allyl groups}$, were also prepared by the action of RMgX on R_FCOOH or R_FCOONa . The results are given in Table I.

The formation of secondary alcohols also accompanied the formation of ketones in many cases. These will be reported in a later paper.

EXPERIMENTAL

The method of Dishart and Levine^{2b} was used in which three moles of the Grignard reagent was treated with one mole of the fluorinated acid (or salt) at temperatures around $0-15^\circ$ for about 5-8 hr. The reaction products were hydrolyzed in hydrochloric acid solution, extracted with ether, dried, and then subjected to fractional distillation.

I. Reaction of $\text{CH}_2=\text{CHCH}_2\text{MgBr}$ and CF_3COONa yielded a mixture of $\text{CF}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}=\text{CH}_2$ and $\text{CF}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{CHCH}_3$ (37.1% yield) collected over a temperature range of $55-80^\circ/623$ mm. This was dried over P_2O_5 , decanted, and then distilled over fresh P_2O_5 whereupon the following fractions were obtained:

Both fractions (A) and (C) gave a positive Baeyer saturation test and a positive haloform reaction with concd. sodium hydroxide. Both are strong lachrymators, but found to have no effect on the respiration or blood pressure of a dog. On standing, fractions (A) and (B) reverted almost entirely to fraction (C) as observed by index of refraction, density, and infrared measurements. A 2,4-dinitrophenylhydrazone of fraction (A) with m.p. $140-141^\circ$ was also prepared (yellow crystals).

Anal. Calcd. for $\text{C}_{11}\text{H}_9\text{F}_3\text{N}_4\text{O}_4$ (2,4 D.N.P. of Fraction (A)): C, 41.52; H, 2.85; F, 17.91. Found: C, 41.30; H, 2.91; F, 18.03.

Infrared absorption spectra of fraction (A) showed one strong carbonyl peak at 5.64μ and a very weak one at 5.78μ ; that of fraction (B) showed two strong peaks in the carbonyl region, one at 5.64μ and another at 5.78μ ; that of fraction (C) showed one strong peak at 5.78μ with a very weak one at 5.64μ . Furthermore, fraction (A) and (B) on standing reverted in all properties (index of refraction, density, infrared spectral data) to those of fraction (C). Hence, we propose

fraction (A) is comprised almost entirely of $\text{CF}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}=\text{CH}_2$, fraction (B) of a mixture of $\text{CF}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}=\text{CH}_2$ and $\text{CF}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{CHCH}_3$, and fraction (C)

almost entirely of $\text{CF}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{CHCH}_3$. The shift in the carbonyl peak from 5.64μ to 5.78μ in going from the β, γ to the α, β isomer is understandable in view of the fact that this results in a shift of the double bond to the conjugate position, hence to greater polarizability of the electrons. Similarly, the higher index of refraction of the α, β isomer over the β, γ isomer is thus accounted for. All three fractions showed strong carbon-carbon double bond absorption at about 6.13μ . Fraction (A) and (B) also showed absorption in the $-\text{OH}$ region (2.85μ). This might find explanation in the fact that some of the β, γ ketone may exist in the enol

form, $\text{CF}_3-\overset{\text{OH}}{\text{C}}=\text{CH}-\text{CH}=\text{CH}_2$. This $-\text{OH}$ absorption

Fraction	Component	B.P./ 623 Mm.	n_D^{20}	d_4^{20}	MR _D		Amount, G.
					Calcd.	Found	
(A)	$\text{CF}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}=\text{CH}_2$	60-61°	1.3544	1.1769	24.83	25.53	5.0
(B)	$\left\{ \begin{array}{l} \text{CF}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}=\text{CH}_2 \\ + \\ \text{CF}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{CHCH}_3 \end{array} \right.$	61-79°	1.3480	—	—	—	11.0
(C)	$\text{CF}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{CHCH}_3$	79-80°	1.3585	1.1891	24.83	25.52	4.0

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disappears for the α, β ketone where enolization is not possible. This, in effect, substantiates the infrared interpretations of Rausch *et al.*,^{2d} who did not obtain and characterize $\text{CF}_3\text{COCH}_2\text{CH}=\text{CH}_2$.

A higher boiling material still remained from the original distillation, and at a pressure of 33-mm. Hg 8.0 g. of a product boiling at 93.0° was obtained. Analysis showed this fraction to be comprised of a higher polymer of the original ketone, $(\text{C}_6\text{H}_5\text{F}_3\text{O})_n$.

This product was yellow in color and possessed a fairly

sweet odor. It gave a positive Baeyer unsaturation test, decolorized aqueous bromine solution, and gave a positive haloform reaction with concd. sodium hydroxide.

II. Reaction of $\text{CH}_2=\text{CHCH}_2\text{MgBr}$ and CF_3COOH yielded results similar to that obtained in I. Reaction of $\text{C}_6\text{H}_5\text{MgBr}$ and $\text{CF}_2=\text{CFCN}$ yielded about 1 g. of material boiling at 100–102° at 5-mm. Hg pressure. This product gave a positive test for unsaturation with 5% permanganate solution and decolorized bromine solution. It formed a 2,4-dinitrophenylhydrazone instantaneously which after two recrystallizations from ethanol-water mixture showed an m.p. 232–234°C.

Anal.: Calculated for $\text{C}_{15}\text{H}_9\text{F}_3\text{N}_4\text{O}_4$: C, 49.19; F, 15.56. Found: C, 49.72; F, 15.80.

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A Qualitative Test for Mono-, Di-, and Tri-substituted Silanes

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The reducing properties of Group IVB metal hydrides have been known and recognized for a long time, but only recently has any use been made of this information.

Buchner¹ reported that silane reduced aqueous silver nitrate to metallic silver. Later, Stock and Somieski² reported the reduction of iron(III), copper(II), and mercury(II) salts to iron(II), copper(I), and copper(0), and mercury(I) and mercury(0), respectively, the degree of reduction being dependent on the original metal ion to silane ratio in the aqueous solution.

Ruff and Albert,³ while investigating the properties of silicochloroform, found it also could function as a reducing agent. They report the reduction of chromium(VI) oxide to chromium(III) oxide, sulfur trioxide to sulfur dioxide, sulfur dioxide to sulfur, arsenic(III) to arsenic(0), and antimony(III) oxide to antimony(0), the latter two in the presence of catalytic amounts of sodium hydroxide. Quite similar results are recorded by Besson and Fournier.⁴

Concomitant with these reductions is the evolution of hydrogen gas. Kipping⁵ devised a method of quantitative analysis for Si-H compounds which involves measurement of the volume of hydrogen produced. His technique entails the dissolution of the silane in an organic base, such as pyridine or piperidine, and measurement of the hydrogen evolved as the mixture is warmed.

The evolution of hydrogen has also served as a

means of monitoring the kinetics of the reaction of Si-H compounds with base. Price⁶ examined the rate of hydrolysis of trialkylsilanes in aqueous alcoholic potassium hydroxide, and found his data agreed satisfactorily with a pseudo first order kinetic expression during the first three fourths of the reaction. In a similar study,⁷ the effect of substituents on the rate of hydrolysis of triarylsilanes in wet piperidine was found to agree well with the values of Hammett's for carbon compounds. The rates of hydrolysis of triphenylsilane-*d* and triphenylsilane-*t* have also been investigated.⁸

The most recent studies of the reducing power of the Group IVB metal hydrides are those reporting the reduction of fourteen different transition metal salts and seven organic acids with triethylgermane,⁹ and the reduction of certain halides and oxides of seven regular group elements and thirteen transitional elements to a lower oxidation state or, in certain cases, to the free element with triethyltin hydride.¹⁰ Another recent publication¹¹ reports the reaction of Si-H compounds with alcohols in the presence of metallic copper. In light of the low yields reported, there exists the possibility that the reaction is indeed catalyzed by oxides of copper and not the metal itself.

In this laboratory, we have had the occasion to synthesize a large number of partially substituted silanes and, while investigating their chemical and physical properties, have developed a sensitive test for the degree of substitution at the silicon atom. Essentially, the test entails treatment of a mixture of one milliliter of a basic solvent, such as pyridine, and two drops of an approximately 5% aqueous solution of copper(II) chloride with one drop of the silane. Monosubstituted silanes discharge the blue color of the test solution within a few seconds and very rapidly thereafter develop a yellow coloration. Disubstituted silanes are somewhat slower in discharging the blue color, giving a final green coloration. The trisubstituted silanes do not discharge the blue color over a period of three minutes. In all cases where color changes were observed, the aryl compound underwent these changes at a more rapid rate than the similarly substituted alkyl compounds. It is possible to differentiate between monoalkyl and monoarylsilanes using nickel(II) salts. Mercury(II) chloride, potassium permanganate, and silver nitrate, more powerful

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