

alcohol was removed by distillation, 20 ml. of water was added and the mixture was extracted several times with ether. The aqueous solution was acidified with sulfuric acid and distilled; the distillate was made alkaline and evaporated to dryness. The residue was converted to isobutyro-*p*-toluidide, m. p. 103.5–104.5°. From the ether extracts there was obtained 0.8 g. of isobutyryl-mesitylene, b. p. 140–143° (20 mm.), n_D^{20} 1.5086, which was converted to α ,3,5-tribromo-2,4,6-trimethylisobutyrophenone, m. p. 106–107°.

Summary

Tetramethyl-1,3-cyclobutanedione has been found to undergo cleavage of the ring when treated with organic magnesium and lithium compounds. The behavior of this cyclic β -diketone has been found to be strictly analogous to the behavior of open-chain β -diketones with these reagents.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Fluorinated Derivatives of Propane and Propylene. VI

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Electron diffraction measurements have shown that atomic distances are shrunk in polyfluorinated groups. This shrinkage is not restricted to the carbon-fluorine distance, but also affects the carbon to chlorine distance in CCl_2F_2 , or the carbon to carbon distance in CF_3CH_3 . To understand the behavior of polyfluorides, it would be well to learn how far this effect extends down a chain, whether the effect of two polyfluorinated groups is cumulative, and what the influence is on a double bond. For such purposes, the synthesis of $\text{CF}_3\text{CH}_2\text{CF}_3$, $\text{CF}_2=\text{CHCF}_3$, $\text{CH}_2=\text{CFCF}_3$ and $\text{CF}_2=\text{CFCF}_3$ was undertaken; these compounds were chosen in the hope that their electron diffraction patterns would not be too complicated to resolve. They were sent to Dr. L. O. Brockway at the University of Michigan, who will report the electron diffraction measurements.

The syntheses have used operations which have all been described in our previous papers.^{1,2,3} All intermediates have been isolated and characterized as single, definite individuals. Great care was given to criteria of purity, for which whole freezing curves, not merely freezing points, were used. Compounds were regarded as adequately purified only after their freezing range had become as small as indicated in the table of physical constants.

Experimental

Synthesis of $\text{CF}_3\text{CH}_2\text{CF}_3$.—The sequence of reactions found most convenient was: $\text{CH}_3\text{CHClCHCl}_2 \rightarrow \text{CH}_3\text{CH}=\text{CCl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CFCl}_2$ and $\text{CH}_3\text{CH}_2\text{CF}_2\text{Cl} \rightarrow \text{CH}_3\text{CH}_2\text{CF}_3$. The starting point was commercial $\text{CH}_3\text{CHClCHCl}_2$, which an alkaline treatment transformed into $\text{CH}_3\text{CH}=\text{CCl}_2$ with an 88% yield. The latter, heated with hydrogen fluoride⁴ at 100° as long as a 20 atm. pressure could be maintained while bleeding off the generated hydrogen chloride, gave an average yield of 60% of $\text{CH}_3\text{CH}_2\text{CF}_2\text{Cl}$ and 12% of $\text{CH}_3\text{CH}_2\text{CFCl}_2$. The passage from $\text{CH}_3\text{CH}_2\text{CF}_2\text{Cl}$ to $\text{CH}_3\text{CH}_2\text{CF}_3$ was easily brought about, in 90% yield, by means of

nascent mercuric fluoride⁵; an alternate method, calling for dehydrohalogenation to $\text{CH}_3\text{CH}=\text{CF}_2$ followed by hydrogen fluoride addition, was found less practical, as its first step proved time-consuming. The trifluoropropane was chlorinated to $\text{CF}_3\text{CH}_2\text{CCl}_3$, in the manner shown before,⁶ and the latter upon treatment with nascent mercuric fluoride⁵ yielded the desired $\text{CF}_3\text{CH}_2\text{CF}_3$ (84%), together with some intermediate $\text{CClF}_2\text{CH}_2\text{CF}_3$, (5%).

Synthesis of $\text{CF}_2=\text{CHCF}_3$.—The hydrogen atoms in $\text{CClF}_2\text{CH}_2\text{CF}_3$ (obtained as shown in the preceding paragraph) are exceedingly acid in character,⁷ and the compound is therefore very easily attacked by alcoholic potassium hydroxide. The action of the alkali removed only hydrochloric acid, as shown by a positive test for chlorine ions and a negative test for fluorine ions. The reaction was both intramolecular, for a 65% yield of $\text{CF}_2=\text{CHCF}_3$, and intermolecular as shown by the appearance of condensation products boiling about 70 and 105°, respectively.

When hydrogen fluoride was added to $\text{CF}_2=\text{CHCF}_3$, practically no $\text{CF}_3\text{CH}_2\text{CF}_3$ was formed at temperatures below 100°, but at 100° or higher the addition proceeded smoothly and quantitatively.

Synthesis of $\text{CH}_2=\text{CFCF}_3$.—The following sequence was used: $\text{CH}_2\text{ClCHClCH}_2\text{Cl} \rightarrow \text{CH}_2=\text{CClCH}_2\text{Cl} \rightarrow \text{CH}_3\text{CFClCH}_2\text{Cl} \rightarrow \text{CH}_3\text{CFClCCl}_2 \rightarrow \text{CH}_3\text{CFClCF}_2\text{Cl} \rightarrow \text{CH}_2=\text{CFCF}_2\text{Cl} \rightarrow \text{CH}_2=\text{CFCF}_3$. The fluorine atom on the central carbon was introduced first. For that purpose, the starting point was commercial $\text{CH}_2\text{ClCHClCH}_2\text{Cl}$, which a caustic treatment transformed into $\text{CH}_2=\text{CClCH}_2\text{Cl}$ in 80% yield. The addition of hydrogen fluoride proceeded normally to give about 70% of $\text{CH}_3\text{CFClCH}_2\text{Cl}$, with $\text{CH}_3\text{CF}_2\text{CH}_2\text{Cl}$ as by-product.⁸ Directed chlorination in sunlight gives the expected $\text{CH}_3\text{CFClCCl}_2$. At this stage, our original plans called for an alkaline treatment to remove hydrogen chloride and yield $\text{CH}_2=\text{CFCCl}_2$, in which the transformation of the CCl_2 group into a CF_3 was expected to be facilitated by its "allylic" character.⁹ However this dehydrohalogenation (and also that of $\text{CH}_3\text{CCl}_2\text{CCl}_3$) failed, because the hydrolysis of $\text{CH}_2=\text{CXCCl}_3$ is much faster than its generation. To avoid this decomposition, partial fluorination of the saturated compound was resorted to, which yielded a mixture of 10% $\text{CH}_3\text{CFClCFCl}_2$, 35% $\text{CH}_3\text{CFClCF}_2\text{Cl}$ and 35% $\text{CH}_3\text{CF}_2\text{CFCl}_2$, separable by distillation. After accumulating $\text{CH}_3\text{CFClCF}_2\text{Cl}$, the alkaline treatment was applied, and yielded very slowly (three days) the desired $\text{CH}_2=\text{CFCF}_2\text{Cl}$, which proved stable enough to resist hydrolysis. In view of the time consumed, the dehydrohalogenation was then tried on $\text{CH}_3\text{CFClCFCl}_2$. When operated under a reflux condenser maintained at about 50°, the olefin $\text{CH}_2=\text{CF}$

(1) Henne in Gilman's "Organic Chemistry," Vol. I, John Wiley and Sons, New York, 1943, p. 944.

(2) Henne in "Organic Reactions," Vol. 2, John Wiley and Sons, New York, 1944, p. 42.

(3) Henne and Waalkes, *THIS JOURNAL*, **67**, 1639 (1945).

(4) Henne and Plueddemann, *ibid.*, **68**, 1271 (1942).

(5) Henne, *ibid.*, **60**, 1569 (1938); Henne and Flanagan, *ibid.*, **65**, 2362 (1943).

(6) Henne and Whaley, *ibid.*, **64**, 1157 (1942).

(7) Henne, Hinkamp and Zimmerschied, *ibid.*, **67**, 1906 (1945).

(8) Henne and Haackl, *ibid.*, **63**, 2692 (1941).

(9) Henne, Whaley and Stevenson, *ibid.*, **62**, 3478 (1941).

TABLE I
PHYSICAL CONSTANTS

Compounds	F. p. range, °C.	F. p., °C.	B. p., °C.	d_{20}^4	n_D^{20}	M. R. ^a	A. R. F. ^b
CH ₃ -CH=CF ₂	0.1	-160.93	-29.0
CF ₂ Cl-CH ₂ -CF ₃	.1	-107	28.4	1.4372	1.2875	21.07	1.13
CF ₂ =CH-CF ₃	.2	-153.11	-21.0
CF ₃ -CH ₂ -CF ₃	.1	-93.62	-0.7
CH ₃ -CFCI-CF ₂ Cl	.4	-30.48	55.6	1.3956	1.3503	25.77	1.09
CH ₂ =CF-CFCl ₂	.4	-115.9 ± 0.2	54.4	1.3523	1.3851	25.48	1.13
CH ₂ =CF-CF ₂ Cl	.4	-143.7	11.9
CH ₂ =CF-CF ₃	.2	-152.24	-28.3
CHCl=CF-CCl ₃	...	Glass	147.8	1.5877	1.4870	35.84	0.77
CHCl=CF-CF ₃	.2	-115.8	15.0
CCl ₂ =CF-CCl ₃	2.0	-77	171.1	1.7064	1.5026	40.21	1.39
CCl ₂ =CF-CF ₃	0.2	-139.6	46.4	1.5389	1.3504	25.60	1.17
CFCl ₂ -CFCl-CF ₃	...	Glass	73.5	1.6643	1.3529	30.92	1.13
CFCl=CF-CF ₃	5.0	-158	7.9
CF ₂ Cl-CFCl-CF ₃	1.0	-136	34.7	1.5896	1.3029	26.21	1.17
CF ₂ =CF-CF ₃	0.4	-156.2	-29.4
CFCl=CCl-CF ₃	.3	-137	47.3	1.5468	1.3511	25.52	1.15
CF ₃ -CFCI-CF ₂	...	Glass	-2.0
CF ₃ CCl ₂ CCl ₂ F		+ 41.74	112.4

^a M. R. is the molecular refraction $\frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2}$. ^b A. R. F. is the atomic refraction for fluorine, computed by subtracting from M. R. the customary increments for C, H, Cl and double bond.

CFCl₂ distilled out as soon as formed and escaped hydrolysis; this procedure gave about 40% of olefin, and 40% of recovered paraffin which was retreated. Both CH₂=CFCl₂ and CH₂=CFCF₂Cl underwent "allylic" fluorination with antimony fluoride in the customary fashion, to yield the desired CH₂=CFCF₃.

Synthesis of CF₂=CFCF₃.—A practical sequence was as follows: CH₃CFClCH₂Cl → CHCl₂CFClCCl₃ → CCl₂=CF-CCl₃ → CCl₂=CFCF₃ → CCl₃CFClCF₃ → CF₂CICClCF₃ → CF₂=CFCF₃. First, commercial CH₃ClCHClCH₂Cl was transformed into CH₃CFClCH₂Cl, as in the preceding paragraph. This was subjected to chlorination but in such a way⁸ as to yield a mixture of CHCl₂CClFCCl₃ and CH₂CICClFCCl₃, from which an alkaline treatment easily gave a mixture of CCl₂=CFCCl₃ and CHCl=CFCCl₃.^{8,10} The two olefins, on "allylic" fluorination⁹ with antimony trifluoride yielded the expected CHCl=CFCF₃ and CCl₂=CFCF₃, both of which were transformed quantitatively into CCl₃CClFCCl₃ by the intensive action of chlorine. This fully chlorinated compound was then fluorinated with SbF₃Cl₂ at 180° to yield about 60% CF₂CICFCICF₃ and 28% CFCl₂CFCICF₃. The last step, zinc treatment of CF₂CICFCICF₃ to yield CF₂=CFCF₃ proved very slow (three days) in boiling alcohol, but was conveniently carried out under pressure at 100°.

Side-line Reactions.—(a) CH₂ClCH₂CF₃ was dehydrohalogenated to yield CH₂=CHCF₃, b. p. -19 to -17°.

(b) CH₃CFClCF₂Cl was treated with zinc but failed to yield more than traces of CH₃CF=CF₂ even at 200°.

(c) CFCl₂CCl₂CF₃ was synthesized from CCl₃CCl₂CF₃ and antimony trifluoride. It was then quantitatively dechlorinated with zinc to CFCl=CClCF₃. Fluorine was

(10) It proved important to prevent the chlorination from reaching the CCl₃CFClCCl₃ stage, because the latter could not be transformed into CCl₂=CFCCl₃ by a zinc treatment and was therefore a total loss; in the zinc treatment much decomposition occurs and an impure product is obtained which seems to contain fluoropentachlorocyclopropane.

added to the double bond by means of the lead dioxide + hydrogen fluoride process³ to yield CF₂CICFCICF₃, from which more CF₂=CFCF₃ was prepared as shown above.

(d) CF₂CICCl₂CF₃⁹ was dehalogenated with zinc to CF₂=CClCF₃, and the latter subjected to fluorine addition³ as in the preceding paragraph, to yield CF₂CFCICF₃.

(e) Hydrogen fluoride addition was tried on a series of olefins. Successful additions were observed with CH₃CH=CF₂ and CF₂=CHCF₃; failures occurred with CHCl=CFCCl₃; CH₂=CFCFCl₂; CH₂=CFCF₂Cl; CH₂=CFCF₃.

Physical Constants.—All compounds were purified in the manner shown in our previous papers,¹¹ and their physical constants were measured¹¹ with the precision denoted in Table I. In this table, the freezing range is that between incipient crystallization and inability further to stir the mass. M. R. is the molecular refraction calculated by means of the Lorenz-Lorentz formula, and A. R. F. is the atomic refraction for fluorine computed by subtracting from M. R. the customary increments for C (2.418), H (1.100), Cl (5.967) and double bond (1.733).

Analysis.—Analyses for chlorine were performed at convenient stages in the various syntheses; the percentages calculated and found were as follows: CF₂CICCl₂CF₃, 21.0 and 20.7; CH₃CFClCF₂Cl, 42.4 and 41.4; CH₂=CF-CFCl₂, 48.2 and 47.8; CCl₂=CFCCl₃, 76.3 and 75.9; CCl₂=CFCF₃, 37.9 and 37.5; CFCl=CFCCl₃, 72.0 and 70.3; CFCl₂CFCICF₃, 44.8 and 44.4.

Summary

For the purpose of interatomic distance measurements a series of new fluorinated derivatives of propane and of propylene have been prepared. Their physical constants were measured after intensive purification and are tabulated.

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(11) Henne and Hinkamp, THIS JOURNAL, **67**, 1194 (1945).