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 isobutyrylmesitylene, b. p. 140–143° (20 mm.), $n^{20}D$ 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

BY ALBERT L. HENNE AND T. PHILLIP WAALKES

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 $CF_3CH_2CF_3$, $CF_2{=}CHCF_3$, $CH_2{=}CFCF_3$ and $CF_2{=}CFCF_3$ 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 $CF_3CH_2CF_3$.—The sequence of reactions found most convenient was: $CH_3CHClCHCl_2 \rightarrow CH_3CH{=}CCl_2 \rightarrow CH_3CH_2CFCl_2$ and $CH_3CH_2CF_2Cl \rightarrow CH_3CH_2CF_3 \rightarrow CCl_3CH_2CF_3 \rightarrow CF_3CH_2CF_3$. The starting point was commercial $CH_3CHClCHCl_2$, which an alkaline treatment transformed into $CH_3CH{=}CCl_2$ with an 88% yield. The latter, heated with hydrogen fluoride[4] 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 $CH_3CH_2CF_2Cl$ and 12% of $CH_3CH_2CFCl_2$. The passage from $CH_3CH_2CF_2Cl$ to $CH_3CH_2CF_3$ was easily brought about, in 90% yield, by means of nascent mercuric fluoride[5]; an alternate method, calling for dehydrohalogenation to $CH_3CH{=}CF_2$ followed by hydrogen fluoride addition, was found less practical, as its first step proved time-consuming. The trifluoropropane was chlorinated to $CF_3CH_2CCl_3$, in the manner shown before,[6] and the latter upon treatment with nascent mercuric fluoride[5] yielded the desired $CF_3CH_2CF_3$ (84%), together with some intermediate $CClF_2CH_2CF_3$, (5%).

Synthesis of $CF_2{=}CHCF_3$.—The hydrogen atoms in $CClF_2CH_2CF_3$ (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 $CF_2{=}CHCF_3$, and intermolecular as shown by the appearance of condensation products boiling about 70 and 105°, respectively.

When hydrogen fluoride was added to $CF_2{=}CHCF_3$, practically no $CF_3CH_2CF_3$ was formed at temperatures below 100°, but at 100° or higher the addition proceeded smoothly and quantitatively.

Synthesis of $CH_2{=}CFCF_3$.—The following sequence was used: $CH_2ClCHClCH_2Cl \rightarrow CH_2{=}CClCH_2Cl \rightarrow CH_3CFClCH_2Cl \rightarrow CH_3CFClCCl_3 \rightarrow CH_3CFClCF_2Cl \rightarrow CH_2{=}CFCF_2Cl \rightarrow CH_2{=}CFCF_3$. The fluorine atom on the central carbon was introduced first. For that purpose, the starting point was commercial $CH_2ClCHClCH_2Cl$, which a caustic treatment transformed into $CH_2{=}CClCH_2Cl$ in 80% yield. The addition of hydrogen fluoride proceeded normally to give about 70% of $CH_3CFClCH_2Cl$, with $CH_3CF_2CH_2Cl$ as by-product.[8] Directed chorination in sunlight gives the expected $CH_3CFClCCl_3$. At this stage, our original plans called for an alkaline treatment to remove hydrogen chloride and yield $CH_2{=}CFCCl_3$, in which the transformation of the CCl_3 group into a CF_3 was expected to be facilitated by its "allylic" character.[9] However this dehydrohalogenation (and also that of $CH_3CCl_2CCl_3$) failed, because the hydrolysis of $CH_2{=}CXCCl_3$ 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% $CH_3CFClCFCl_2$, 35% $CH_3CFClCF_2Cl$ and 35% $CH_3CF_2CFCl_2$, separable by distillation. After accumulating $CH_3CFClCF_2Cl$, the alkaline treatment was applied, and yielded very slowly (three days) the desired $CH_2{=}CFCF_2Cl$, which proved stable enough to resist hydrolysis. In view of the time consumed, the dehydrohalogenation was then tried on $CH_3CFClCFCl_2$. When operated under a reflux condenser maintained at about 50°, the olefin $CH_2{=}CF$-

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(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 Plueddeman, *ibid.*, **65**, 1271 (1943).

(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 Haeckl, *ibid.*, **63**, 2692 (1941).

(9) Henne, Whaley and Stevenson, *ibid.*, **63**, 3478 (1941).

TABLE I

PHYSICAL CONSTANTS

Compounds	F. p. range, °C.	F. p., °C.	B. p., °C.	d^{20}_4	n^{20}_D	M. R.[a]	A. R. F.[b]
$CH_3-CH=CF_2$	0.1	−160.93	−29.0	....	....	...	..
$CF_2Cl-CH_2-CF_3$	.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	....	....	...	..
$CH_3-CFCl-CF_2Cl$	.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
$CH_2=CF-CF_2Cl$	.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	....	....	...	..
$CF_2Cl-CFCl-CF_3$	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
$CF_3-CFCl-CF_3$	...	Glass	−2.0	....	....	...	..
$CF_3CCl_2CCl_2F$		+ 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.

$CFCl_2$ 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 $CH_2=C$-$FCFCl_2$ and $CH_2=CFCF_2Cl$ underwent "allylic" fluorination with antimony fluoride in the customary fashion, to yield the desired $CH_2=CFCF_3$.

Synthesis of $CF_2=CFCF_3$.—A practical sequence was as follows: $CH_3CFClCH_2Cl \rightarrow CHCl_2CFClCCl_3 \rightarrow CCl_2=CF$-$CCl_3 \rightarrow CCl_2=CFCF_3 \rightarrow CCl_3CFClCF_3 \rightarrow CF_2ClCClFCF_3 \rightarrow CF_2=CFCF_3$. First, commercial $CH_2ClCHClCH_2Cl$ was transformed into $CH_3CFClCH_2Cl$, as in the preceding paragraph. This was subjected to chlorination but in such a way[8] as to yield a mixture of $CHCl_2CClFCCl_3$ and $CH_2ClCClFCCl_3$, from which an alkaline treatment easily gave a mixture of $CCl_2=CFCCl_3$ and $CHCl=CFCCl_3$.[8,10] The two olefins, on "allylic" fluorination[9] with antimony trifluoride yielded the expected $CHCl=CFCF_3$ and $CCl_2=CFCF_3$, both of which were transformed quantitatively into $CCl_3CClFCF_3$ by the intensive action of chlorine. This fully chlorinated compound was then fluorinated with SbF_3Cl_2 at 180° to yield about 60% $CF_2ClCFClCF_3$ and 28% $CFCl_2CFClCF_3$. The last step, zinc treatment of $CF_2ClCFClCF_3$ to yield $CF_2=CFCF_3$ proved very slow (three days) in boiling alcohol, but was conveniently carried out under pressure at 100°.

Side-line Reactions.—(a) $CH_2ClCH_2CF_3$ was dehydrohalogenated to yield $CH_2=CHCF_3$, b. p. −19 to −17°.

(b) $CH_3CFClCF_2Cl$ was treated with zinc but failed to yield more than traces of $CH_3CF=CF_2$ even at 200°.

(c) $CFCl_2CCl_2CF_3$ was synthesized from $CCl_3CCl_2CF_3$ and antimony trifluoride. It was then quantitatively dechlorinated with zinc to $CFCl=CClCF_3$. Fluorine was added to the double bond by means of the lead dioxide + hydrogen fluoride process[3] to yield $CF_2ClCFClCF_3$, from which more $CF_2=CFCF_3$ was prepared as shown above.

(d) $CF_2ClCCl_2CF_3$[9] was dehalogenated with zinc to $CF_2=CClCF_3$, and the latter subjected to fluorine addition[3] as in the preceding paragraph, to yield $CF_3CFClCF_3$.

(e) Hydrogen fluoride addition was tried on a series of olefins. Successful additions were observed with $CH_3CH=CF_2$ and $CF_2=CHCF_3$; failures occurred with $CHCl=CFCCl_3$; $CH_2=CFCFCl_2$; $CH_2=CFCF_2Cl$; $CH_2=CFCF_3$.

Physical Constants.—All compounds were purified in the manner shown in our previous papers,[11] and their physical constants were measured[11] 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: $CF_2ClCH_2CF_3$, 21.0 and 20.7; $CH_3CFClCF_2Cl$, 42.4 and 41.4; $CH_2=CF$-$CFCl_2$, 48.2 and 47.8; $CCl_2=CFCCl_3$, 76.3 and 75.9; $CCl_2=CFCF_3$, 37.9 and 37.5; $CFCl=CFCCl_3$, 72.0 and 70.3; $CFCl_2CFClCF_3$, 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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(10) It proved important to prevent the chlorination from reaching the $CCl_3CFClCCl_3$ stage, because the latter could not be transformed into $CCl_2=CFCCl_3$ 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.

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