JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 67 AUGUST 9, 1945 NUMBER 8

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

Fluorinated Derivatives of Cyclopentene and Cyclopentane

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The fluorination of $CCl_3CCl{=}CCl_2$ to $CF_3CCl{=}CCl_2$ is exceedingly easy because the CCl_3 group is made "allylic" by the double bond once removed.[1] This activating effect is not restricted to just one group: in $(CCl_3)_2C{=}C(CCl_3)_2$, the chlorine atoms are all "allylic."

Activation on both sides of a double bond applies also to cyclic compounds. From perchlorocyclopentene $CCl{=}CClCCl_2CCl_2CCl_2$ and SbF_3, Whaley[2] prepared a tetrafluoride $C_5F_4Cl_4$ which he later transformed into a hexafluoride $C_5F_6Cl_2$ by means of mercuric fluoride. He logically postulated the formulas to be $CCl{=}CClCF_2CCl_2CF_2$ and $CCl{=}CClCF_2CF_2CF_2$, respectively. The compounds were not described further, so a repetition of Whaley's experiment became the starting point of our work.

The fluorination was performed with antimony trifluoride to which 5–10% of SbF_3Cl_2 had been added, as we had noted that (in small amounts) the latter salt would not chlorinate the double bond in C_5Cl_8, and could therefore be used for its customary accelerating effect. Unexpectedly, the main reaction product was found to be a hexafluoride instead of the tetrafluoride mentioned by Whaley. Moreover, when the tetrafluoride was refluorinated, it was converted chiefly to a penta and a hexafluoride, but also to a trifluoride, thus indicating disproportionation by "redistribution."[3]

For the tetrafluoride, the formula postulated by Whaley was quite acceptable. For the hexafluoride, the formula had to be demonstrated. Whaley's hexafluoride was not available for comparison, and identity of his preparation and ours could not be postulated. In the tetrafluoride $CCl{=}CClCF_2CCl_2CF_2$, all the chlorine atoms were expected to be hard to replace, because two of them are vinylic, while the other two are adjacent to a CF_2 group.[4] Oxidation to perfluoroglutaric acid, $HO_2C(CF_2)_3CO_2H$, proved that the hexafluoride formula was $CCl{=}CClCF_2CF_2CF_2$.

The unexpectedly easy passage from the tetrafluoride to the hexafluoride may be due to the fact that the activating effect of the double bond extends beyond the "allylic" position. Experiments are now under way to ascertain this point.

Saturation of the double bond in cyclo-$C_5F_6Cl_2$ by means of two halogen atoms proved exceedingly difficult. Reaction with SbF_5[5] caused the formation of very little $CClFCClFCF_2CF_2CF_2$, and even smaller quantities of cyclo-C_5F_9Cl and cyclo-C_5F_{10}. Reaction with SbF_3Cl_2 was practically nil. Only in ultraviolet illumination and at a temperature of 70° did the addition of gaseous chlorine take place, but under these conditions the reaction yielded $CCl_2CCl_2CF_2CF_2CF_2$ quantitatively. All efforts to fluorinate this saturated compound failed. This failure was well in line with the difficulty, noted above, of exchanging halogens on a carbon adjacent to a CF_2 group.

Experimental

Fluorination of Perchlorocyclopentene.—Nine moles (1800 g.) of powdered antimony trifluoride was placed in a steel vessel fitted with a pressure gage and a needle valve. The vessel was evacuated, and about 5% of chlorine by weight was allowed to be absorbed by connecting with a chlorine tank. Then three moles (1020 g.) of octachlorocyclopentene,[6] C_5Cl_8, was added. The reagents were mixed

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(1) Henne, Whaley and Stevenson, THIS JOURNAL, **63**, 3478 (1941).

(2) Private communication; present address, 600 Capitol Place, Columbia, S. C.

(3) Calingaert in Gilman's "Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 1806.

(4) Henne and Flanagan, THIS JOURNAL, **65**, 2362 (1943).

(5) Ruff, *Ber.*, **69A**, 181 (1936).

(6) Prins, *Rec. Trav. Chim.*, **57**, 659 (1938).

TABLE I

PHYSICAL CONSTANTS

		F. p., °C.	B. p., °C.	d^{20}_4	n^{20}_D	*MR*	*ARF*
1	$CCl{=}CClCFClCCl_2CCl_2$		116–118 (10 mm.)		1.546		
2	$CCl{=}CClCFClCCl_2CFCl$		90–93 (10 mm.)		1.513		
3	$CCl{=}CClCF_2CCl_2CFCl$		185–190		1.48		
4	$CCl{=}CClCF_2CCl_2CF_2$	glass	155.19	1.7165	1.4429	42.91	1.30
5	$CCl{=}CClCF_2CFClCF_2$	glass	122.98	1.6852	1.4069	38.17	1.29
6	$CCl{=}CClCF_2CF_2CF_2$	−105.82	90.72	1.6546	1.3676	33.30	1.26
7	$CCl_2CCl_2CF_2CF_2CF_2$	151 to 153	sublimes				
8	$C_3F_6(CO_2H)_2$	78 to 88	134–138 (3 mm.)				
9	$C_3F_6(CO_2CH_3)_2$	−31.8 to −33.6	100.0–100.3 (34 mm.)	1.4856	1.3518	38.99	1.33

by shaking. The vessel was heated overnight on a steam-bath. This brought the pressure to about 10 atmospheres. Heating with a free flame was substituted, and distillation was allowed through the needle valve at such rate that the pressure remained about 10 atmospheres. The distillate was led into a water scrubber followed by two ice traps. The distillate in the three traps was united, steam distilled and rectified to obtain 28 g. of heads, 360 g. (1.50 mole) of hexafluoride $C_5F_6Cl_2$, and 177 g. of a mixture of $C_5F_5Cl_3$ and $C_5F_4Cl_3$. The conversion to the hexafluoride was thus 50%, and the material accounted for 78%.

By varying the proportions of reagents, the tetrafluoride could be made the chief reaction product, but it was invariably accompanied by less fluorinated intermediates. Refluorination of the intermediates always showed disproportionation. For example, the refluorination of 2.6 moles of $C_5F_5Cl_3$ gave 1.28 moles of $C_5F_6Cl_2$, 0.75 mole of $C_5F_5Cl_3$, 0.26 mole of $C_5F_4Cl_4$ and 0.17 mole of $C_5F_3Cl_5$.

Oxidation of Cyclo-$C_5F_6Cl_2$ to Perfluoroglutaric Acid.—The ring of the hexafluoride was opened by alkaline oxidation in the manner previously reported,[7] in accordance to the reaction: $3C_5F_6Cl_2 + 4KMnO_4 + 8KOH \rightarrow 3C_3F_6(CO_2K)_2 + 4MnO_2 + 6KCl + 4H_2O$. In a three-liter, three-necked flask equipped with a mercury-sealed stirrer, a six-bulb reflux condenser, and heated in a water-bath, were placed 0.5 mole (123 g.) of $C_5F_6Cl_2$, the theoretical amount (105 g.) of potassium permanganate, 75 g. of potassium hydroxide and 500 ml. of water. After the mixture had refluxed for twelve hours, it was subjected to steam distillation, which allowed the recovery of 22 g. of the original hexafluoride. The reaction mixture was then acidified with 210 ml. of concentrated sulfuric acid in 250 ml. of water. Sulfur dioxide was bubbled through the solution until all the manganese dioxide was reduced. The perfluoroglutaric acid was then continuously extracted with ether. After drying the extract over calcium chloride, the ether was distilled off, leaving a solid residue. Distillation through a small Vigreux yielded 246 g. of a white crystalline acid, m. p. 78–88°, b. p. 134–138 (3 mm.). This was an 86% yield. The acid was very hygroscopic; its neutral equivalent of 119.5 corresponded to a molecular weight of 239 (theory 240); fluorine content 47.3% (theory 47.5%). It was insoluble in benzene, but soluble in acetone.

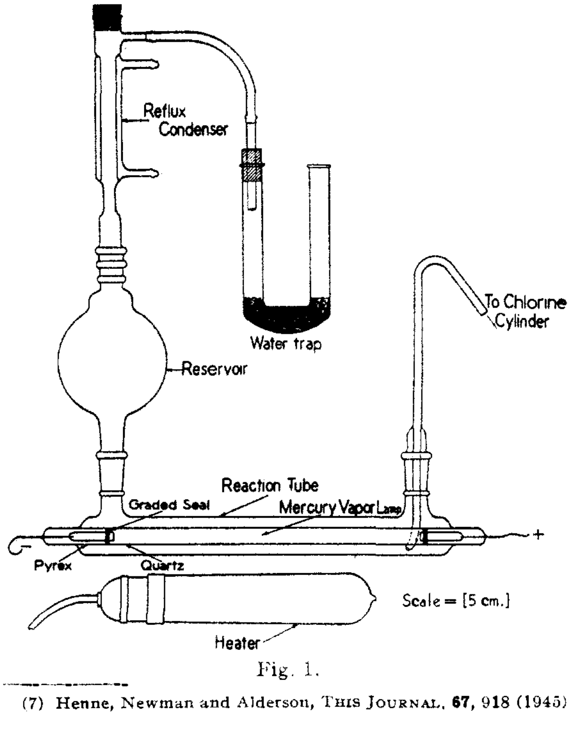

Fig. 1.

Dimethyl perfluoroglutarate was made by dissolving 106 g. of acid in 800 ml. of absolute methanol then bubbling a stream of dry hydrogen chloride through the mixture. After forty-two hours of refluxing, most of the excess of methanol was removed through a Vigreux column. The residue was dissolved in ether, washed with dilute sodium carbonate, then a saturated solution of calcium chloride, and filtered through anhydrous sodium sulfate. Rectification at 87° (19 mm.) gave 77 g. of diester. From the carbonate solution, 20 g. of perfluoroglutaric acid was recovered by acidifying and extracting with ether. Based on the amount of acid consumed, the esterification yield was 80%. The ester was then rectified through a seven-plate column.

Treatment of Cyclo-$C_5F_6Cl_2$ with Antimony Pentafluoride.—In the hope of adding 2 atoms of fluorine to the double bond, two moles of SbF_5[6] were heated in a steel container with 1.5 moles of $C_5F_6Cl_2$, first for twenty-four hours at 105° which brought the pressure up to 8 atm., then with a free flame to reach 15 atm. The reaction products were fractionated to give the following fractions (end b. p., weight, refractive index): 37°, 4 g., 1.28; 40°, 4 g., 1.28; 57°, 21 g., 1.295 (C_5F_9Cl); 60°, 10 g., 1.3095; 83°, 17 g., 1.3308; 88°, 20 g., 1.3498 ($C_5F_8Cl_2$); 92°, 199 g., 1.3644 ($C_5F_6Cl_2$); 92°, 8 g., 1.3667; residue, 19 g., 1.3835. The results were thus disappointing.

Chlorination of Cyclo-$C_5F_6Cl_2$ to Cyclo-$C_5F_6Cl_4$.—Even in brilliant sunshine, $C_5F_6Cl_2$ failed to absorb much chlorine. An apparatus was then constructed (see Fig. 1) which consisted of a mercury arc in a quartz tube immersed in the liquid to be chlorinated. A carbon filament lamp was used to keep the liquid warm. Under these conditions, addition of chlorine proceeded quantitatively. To avoid high losses, the handling of the chlorinated prod-

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[7] Henne, Newman and Alderson, THIS JOURNAL, **67**, 918 (1945).

uct requires precautions, because it is a solid with an exceedingly high vapor tension.

Fluorination of Cyclo-$C_5F_6Cl_4$.—Fluorination with SbF_3Cl_2, as well as with a mixture of HgO + HF, was fruitless, and the starting material was recovered intact.

Summary

Octachlorocyclopentene was fluorinated as far as the hexafluoride cyclo-$C_5F_6Cl_2$ in one operation. The formula of the latter was demonstrated to be $\overline{CCl{=}CClCF_2CF_2C}F_2$ by opening the ring to yield perfluoroglutaric acid. Halogenation of the double bond of cyclo-$C_5F_6Cl_2$ was found exceedingly difficult, but chlorination was performed quantitatively in ultraviolet light, at 70°. The resulting cyclo-$C_5Cl_4F_6$ resisted all attempts at further fluorination.

COLUMBUS, OHIO RECEIVED[8] MAY 7, 1945

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[8] This manuscript was originally received on July 10, 1944, and after examination by the editorial board was accepted for publication in THIS JOURNAL. It was, however, referred to the National Defense Research Committee and at their request was withheld from publication, in a confidential file, until clearance was granted on May 5, 1945.

[CONTRIBUTION OF THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Preparation of Cyclopentenes and Cyclopentanes. I[1]

BY GRANT CRANE,[2] CECIL E. BOORD AND ALBERT L. HENNE

In the course of a search for methods for the large scale preparation of monoalkylcyclopentanes, three procedures have been investigated: (1) condensation of an allylic chlorocyclopentene with a Grignard reagent to give an alkylcyclopentene which can be hydrogenated; (2) condensation of cyclopentanone with a Grignard reagent to yield an alkylcyclopentanol which can be dehydrated, then hydrogenated; (3) condensation of cyclopentadiene and a ketone to a fulvene derivative, and hydrogenation of the latter

Intermediate compounds, when not previously described in the literature, have been characterized, and additional data have been given for compounds already known.

First Method.—3-Chlorocyclopentene, prepared by 1,4-addition of hydrogen chloride to cyclopentadiene,[3,4] reacts with aryl-[5] or alkylmagnesium halides[6,7] to give 3-substituted cyclopentenes. The yields, based on the original cyclopentadiene, Table Ia, were 23–48% with primary alkylmagnesium halides, 20–27% with secondary, and only 2% with tertiary butylmagnesium chloride. Yields were slightly better with chlorides than with bromides. Reactions performed in copper vessels gave yields slightly better than in glass and distinctly better than in steel. Reversing the order of the addition, *i. e.*, adding the Grignard reagent to the 3-chlorocyclopentene, lowered the yields from 34–41% to 9–16%, in the case of propylmagnesium bromide.

TABLE Ia

3-ALKYLCYCLOPENTENES

R-Mg-X	Moles R-Mg-X	Moles C_5H_7Cl	Reaction vessel	Yield, %
Me-Mg-Cl	12	8.7	Copper	23.7
Et-Mg-Cl	12	8.5	Copper	48.3
Et-Mg-Br	3.7	3.0	Glass	42.7
n-Pr-Mg-Cl	20	14.1	Copper	47.5
n-Pr-Mg-Br	18	14.6	Iron	17.8
n-Pr-Mg-Br	8	7.34	Glass	37.9
n-Pr-Mg-Br	12	9.32	Copper	41.1
n-Pr-Mg-Br	11	8.95	Copper	15.6[a]
i-Pr-Mg-Cl	12	9.2	Copper	27.6
i-Pr-Mg-Br	3.7	3.7	Glass	20.0
n-Bu-Mg-Br	5	3.1	Glass	46.3
i-Bu-Mg-Br	5	3.1	Glass	39.0
s-Bu-Mg-Br	18	13.7	Copper	23.7
t-Bu-Mg-Br	18	14.2	Copper	2.0

[a] Order of addition reversed.

Ozonolysis of the alkylcyclopentenes yielded α-alkyl glutaric acids, showing that the side chains are in the 3-position. Table Ib lists the physical properties of the 3-alkylcyclopentenes produced. All were hydrogenated to the corresponding alkylcyclopentanes, the properties of which are summarized in Table II.

TABLE Ib

3-ALKYLCYLCOPENTENES

Alkyl group	B. p., °C. 760 mm.	d^{20}_4	n^{20}_D	M. R. L. and L.	M. R. Calcd.
Methyl-	64.9	0.7622	1.4207	27.29	27.24
Ethyl-	98.1	.7830	1.4321	31.85	31.86
n-Propyl-	125.9	.7910	1.4359	36.38	36.48
i-Propyl-	121.2	.7941	1.4380	36.40	36.48
n-Butyl-	151.6	.7990	1.4407	41.03	41.10
s-Butyl-	149.7	.8092	1.4464	40.97	41.10
i-Butyl-	143.6	.7936	1.4393	41.19	41.10
t-Butyl-	139.1	.8066	1.4430	40.83	41.10

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[1] This paper represents a part of the dissertation submitted by Grant Crane to the Graduate School of Ohio State University in partial fulfillment of the requirements for the Ph.D. degree. Presented in part before the Organic Division of the American Chemical Society at the Detroit meeting, September 11, 1940.

[2] Research Assistant of the staff of the American Petroleum Institute Hydrocarbon Research Project at Ohio State University. Grateful acknowledgment is made for the support received, from the above project, for this work. Presently, Lieutenant Colonel, U. S. Marines, Pacific Theatre.

[3] Kraemer and Spilker, *Ber.*, **29**, 552 (1896).

[4] Noeldechen, *ibid.*, **33**, 3348 (1900).

[5] v. Braun and Kuhn, *ibid.*, **60B**, 2551 (1927).

[6] v. Braun, Kamp and Kopp, *ibid.*, **70B**, 1753 (1937).

[7] Plate, *Compt. rend. acad. sci. U. R. S. S.*, **24**, 257 (1939) (in English).