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

The Addition of Fluorine to Double Bonds

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For the synthesis of organic fluorides, all the classical methods of fluorination may be used, yet some are more practical than others.[1] The addition of fluorine to double bonds has been observed in only few cases, and is very impractical because the large amount of heat evolved breaks down the organic material.[1] We present now a procedure which consists essentially in generating nascent lead tetrafluoride inside the olefinic compound to be fluorinated, and simultaneously permitting it to decompose into lead difluoride and a molecule of fluorine to be accepted by the olefin.

The use of lead tetrafluoride has been claimed by Dimroth and Bockemüller[2] who prepared it from lead tetraacetate, then allowed it to react with diphenyl-ethylene for a 42% yield of $(C_6H_5)_2CFCH_2F$. We failed in our efforts to repeat this work, as the preparation of good lead tetrafluoride could not be mastered, while the reaction of impure preparations turned out indifferent results.

To skirt the difficulties, we devised a new procedure as follows. At a temperature of −78°, we place into a sturdy metal vessel a mixture of lead dioxide, hydrogen fluoride and an excess of olefinic material and close the vessel while the reaction mixture is cold; when the temperature rises, a vigorous reaction takes place which ends in a few minutes; this reaction evolves much heat and generates a temporary pressure which may be quite high; the result is a mixture of the difluoride in an excess of the original material, which in most cases is easily separable by distillation.

As shown in the table, the reaction was tried on seven different olefins and succeeded each time. The investigation was conducted in a way to determine primarily the scope of the reaction, and the perfection of the experimental details to obtain better yields was left for later research. It was, however, found that no fluorination occurred when lead dioxide was slowly "dusted" into a solution of hydrogen fluoride in an excess of olefin, kept about 20 to 25°. The experimental procedure used was that recommended for the mercuric oxide and hydrogen fluoride technique,[3,4] *i. e.*, operation in a sealed steel vessel capable of withstanding a pressure of 10 to 12 atmospheres. Unless better devices are provided to guard against the high pressure momentarily developed, it is safer not to operate on quantities involving more than one mole of lead dioxide.

In Table I the conversion percentage refers to the quantity of fluorine addition product actually isolated, while the yield percentage is computed after subtracting the amount of recovered olefin from the quantity originally used. Both quantities are computed relative to the organic material involved.

Some of the compounds so produced were known, and their physical properties were found to agree exactly with the known values, thus proving that the reaction is one of addition. The compounds which are new are described in our following paper; they were analyzed for chlorine and found correct within 0.3%: $CF_3CClFCClF_2$, 44.8 calcd. and 44.5 found; $CHClFCHClF$, 52.6 and 52.5; $CF_3CClFCCl_2F$, 32.1 and 32.3; $CF_3CClFCF_3$, 17.4 and 17.1; $CF_3CF_2CFCl_2$, 32.1 and 31.9.

TABLE I

EXPERIMENTAL RESULTS

Olefin	Moles of olefin treated	Moles of HF	Moles of PbO_2	Ratio HF/PbO_2	Reaction product	% Conversion	% Net yield
$CF_3CCl{=}CCl_2$	1.0	10	1	10/1	$CF_3CClFCCl_2F$	22.3	30
	2.0	23	2.3	10/1		19.6	30
	1.5	26	1.55	16.7/1		37.3	57.7
	1.3	26	1.3	20/1		42.3	59.1
	3.0	60	3.0	20/1		16.3	33
$CF_3CCl{=}CFCl$	0.3	4.5	0.3	15/1	$CF_3CClFCClF_2$	19	42
	0.75	15	0.75	20/1		14	25.3
$CCl_2{=}CCl_2$	2	28	2	14/1	CCl_2FCCl_2F	38	58.5
$CHCl{=}CCl_2$	2	27	2.2	12/1	$CHClFCCl_2F$	18	27.7
	0.5 in $CHCl_3$	10	0.5	20/1		19	32.4
$CHCl{=}CHCl$	0.75 in CCl_4	15	0.75	20/1	$CHClFCHClF$	16	17.1
$CF_3CCl{=}CF_2$	1.6	18	1.8	10/1	$CF_3CClFCF_3$	14	20
	1.0	21	1.0	21/1		10	12 (accident)
$CFCl_2CF{=}CF_2$	0.6	6.8	0.68	10/1	$CFCl_2CF_2CF_3$	11	24

An obvious advantage of fluorine addition is the possibility of synthesizing symmetrical compounds, such as $CHClFCHClF$. Fluorinated derivatives of ethane previously described are

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(1) Henne in "Organic Reactions," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1944.

(2) Dimroth and Bockemüller, *Ber.*, **64**, 516 (1931).

(3) Henne, THIS JOURNAL, **60**, 1569 (1938).

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

preponderantly unsymmetrical compounds, because their synthesis hinges directly or indirectly on addition of a hydrogen halide to a double bond; for instance, fluorination of symmetrical $CHCl_2$-$CHCl_2$ with antimony trifluoride or hydrogen fluoride leads to asymmetrical CHF_2CHCl_2, then CF_3CH_2Cl.[5]

In each reaction, it was noted that some low boiling material was invariably present. This was taken as an indication that some halogen substitution had taken place, probably at the expense of the lead difluoride, and should be investigated further as it may lead to a more efficient utilization of the total fluorine available in the reaction.

In addition to the reactions listed in the table, one diene was subjected to the lead dioxide and hydrogen fluoride treatment. Perchlorobutadiene $CCl_2{=}CClCCl{=}CCl_2$, $n^{20}D$ 1.5542 gave a reaction product with a refractive index of 1.492 and an analysis which corresponded to a formula $C_4Cl_6F_2$ (Cl: found 69.6%, calcd. 71.2%). This compound discolored permanganate, and can therefore be represented by only two formulas, $CFCl_2$-$CClFCCl{=}CCl_2$ or $CFCl_2CCl{=}CClCFCl_2$, which correspond to the fluorination of only one of the two double bonds, by 1,2- or by 1,4- addition, respectively. This difluoride reacted readily with zinc, with the loss of chlorine only, a fact which seems to favor the first formula.

Summary

Addition of fluorine to an olefinic double bond has been achieved by interaction of lead dioxide with hydrogen fluoride in the olefin which is to receive the fluorine. The reaction makes nascent lead tetrafluoride, which decomposes into lead difluoride and a mole of fluorine which is accepted by the olefinic double bond.

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(5) Henne and Renoll, THIS JOURNAL, **58**, 887 (1936).

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Activation of Passive Iron in Chromic–Sulfuric–Nitric Acid Solution by Rapid Rotation

BY W. H. CONE AND DON H. ANDERSON

The existence of passive iron was reported over one hundred and fifty years ago. Passivity is an intriguing phenomenon and one of fundamental importance. Each year a new series of papers with new approaches to this problem appears. Much disagreement exists among various investigators and probably will continue until it is recognized by all that passivity may be due to a number of factors and that it may be destroyed in many ways.

There are certain important points on which most investigators agree: one, that the passivating agents, whatever they may be, are capable of depositing on a piece of iron a film whose exact nature is unknown; second, a sample of passive iron tends to lose its passivity at higher temperatures in passivating solutions; third, most passivating agents are oxidants; fourth, any condition which can destroy the protective film is capable of causing activation.

It was shown[1] that iron could be made active in chromic acid solutions by reducing the pressure before immersing the iron in the solution. It was believed that the primary cause of passivity was an adsorbed layer of oxygen on the iron and that the reduction in pressure altered this layer to such an extent that the chromic acid was able to attack the metal. Since no gas was evolved in this reaction, no gas film could be formed and once active the iron continued to dissolve.

Experimental

The solution had the composition: CrO_3 51.0%; H_2SO_4 6.3%; H_2O 42.2%; HNO_3 0.5% and is hereinafter called the chromic acid solution. The chemicals were all analytical reagent grade. The iron rod in most of the experiments was a soft commercial iron having a diameter of 5 mm. and a length of 120 mm. However, a few check runs were made using J. T. Baker Co. "Iron Wire for Standardizing" which was wound around a glass rod to give rigidity. The vessel containing the solution was provided with two side arms for insertion of a potassium nitrate–agar bridge and a thermometer. The potential of the rod was measured against a normal calomel half cell. Immediately before each run the rod was polished with fine emery paper. Runs were made by placing the rod in the chromic acid solution and increasing the speed of the motor until the potentiometer reading indicated that the iron was active.

The speed of the rotating rod was determined either by a tachometer or by a stroboscope.

The rotational speed necessary to produce activation appears to be dependent on the turbulence in the solution. The data for a smoothly rotating rod are shown in Table I and curve A in Fig. 1.

TABLE I

ACTIVATING SPEED FOR ROD RUNNING ON CENTER

Temp., ° C.	5.0	12.0	22.4	25.5
R. p. m.	12200	11900	8100	8600
Temp., ° C.	26.0	26.5	34.0	37.8
R. p. m.	8140	7690	7675	6400

The data in Table II and Curve B, Fig. 1, are for a rod bent so that the moving tip was 2 mm. offset from the axis of rotation. This produced considerable turbulence in the solution and caused activation at considerably lower speeds.

TABLE II

ACTIVATING SPEED FOR ECCENTRIC ROD

Temp., ° C.	1.0	5.5	8.1	8.9	11.1	15.2	19.8	22.1
R. p. m.	4450	4600	4740	4400	4030	2620	2940	3250
Temp., ° C.	23.2	23.3	26.2	27.1	27.5	28.7	29.1	31.0
R. p. m.	3290	3300	2925	2890	2820	2750	2700	2650

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(1) Cone and Tartar, THIS JOURNAL, **59**, 937 (1937).