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The Action of Elementary Fluorine upon Organic Compounds. XXIII. The Jet Fluorination of Certain Aliphatic Hydrocarbons as Oriented and Controlled by Operating Conditions[1]

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The simple continuous jet fluorination of methane, ethane, propane, *n*-butane. isobutane and neopentane has been carried out; and the orientation of these fluorinations in the direction of simple products in acceptable yields as controlled by the operating conditions has been studied. The average optimum percentage yields in the several groups of products were: perfluoro 87, monohydro 49, dihydro isomers 35, trifluoro (1 compound) 44, difluoro 31 and monofluoro 40. The new pure compound $(CF_3)_3C-CHF_2$, a subliming solid, m.p. 69° (sealed tube), b.p. (5.3 atm.) 96–97°, has been isolated. The original jet reactor has been considerably modified, and a new triple jet reactor designed for very mild fluorinations has been described.

In an earlier paper[4] there was described a new jet fluorination reactor originally designed by Tyczkowski in this Laboratory, in which the diluted sample was introduced through a turbulent jet into an atmosphere of fluorine, itself diluted with reactor gases circulated by jet pump action.

This paper describes the application of this simple continuous jet process to the direct fluorination of methane, ethane, propane, *n*- and isobutane and neopentane, as well as the orientation of these fluorinations in the direction of simple products in acceptable and often excellent yields, through the adequate control of the operating conditions employed. The original reactor has been modified considerably during the course of this work, and a new triple jet reactor introduced, especially designed for very mild fluorinations in which both the sample and the fluorine were admitted to the reaction zone through turbulent jets.

Before discussing the influence of experimental conditions upon these fluorinations, it appears desirable to present the optimum yields of the various types of fluorinated products which have been obtained from the hydrocarbons studied, and these will be found collected in Table I, in which the values are expressed in liquid volume per cent. of the total condensate in each case.

TABLE I

THE JET FLUORINATION OF ALIPHATIC HYDROCARBONS ORIENTATION TOWARD INDIVIDUAL STRUCTURES

Highly fluorinated

Hydrocarbon	Perfluoro compound	Monohydro-R_FH	Dihydro-R_FH_2 (isomers)
C_2H_6	C_2F_6, 87	CF_3CHF_2, 70	....
C_3H_8	C_3F_8, 85	$C_2F_5CHF_2$, 46	$C_3H_2F_6$, 50
n-C_4H_{10}	*n*-C_4F_{10}, 89	....	....
$(CH_3)_3CH$	$(CF_3)_3CF$, 88	$(CF_3)_2CFCHF_2$,[a] 41	$C_4H_2F_8$, 35
$(CH_3)_4C$	....	$(CF_3)_3CCHF_2$, 39	$C_5H_2F_{10}$, 21

Partially fluorinated

Hydrocarbon	Trifluoro-RF_3	Difluoro-RF_2	Monofluoro-RF
CH_4	....	CH_2F_2, 45	CH_3F,[b] 67
C_2H_6	CHF_2CH_2F, 44	CH_3CHF_2, 17	CH_3CH_2F, 42
C_3H_8	....	....	$C_2H_5CH_2F$, 11

[a] Most probable structure. [b] Recycling required.

From this it will be seen that the ranges in percentage yields in the several groups were: perfluoro 89–85, monohydro 70–39, dihydro isomers 50–21, trifluoro (1 compound) 44, difluoro 45–17 and monofluoro 67–11, respectively.

It is of interest that no perfluoro neopentane $(CF_3)_4C$ was obtained under any of the conditions currently studied, which was presumably due to the great electrical and steric hindrance produced by the sheath of fluorine atoms surrounding the molecule of the monohydro derivative. The former compound, m.p. 78.3° (sealed tube), has been prepared by Dresdner[5] by an entirely different method involving co-pyrolysis at very high temperatures. The fluorinated neopentane prepared in this work consisted mostly of subliming solids, which could not be separated effectively either by rectification at 2 atm. pressure, or by fractional sublimation. It could, however, readily be distilled at 5–6 atm. pressure in a small all-glass unit equipped with a Vigreux column and remote controlled stopcock, and completely contained in a large metal box with a safety glass front, maintained at an internal temperature sufficient to keep the sample liquid, or about 50°. Under these conditions a fraction was obtained corresponding to the new compound $(CF_3)_3C-CHF_2$, b.p. 96–97° at 5.3 atm., m.p. 69° (sealed tube), mol. wt. 259–261 (calcd. 260). Both the melting point and vapor pressure were lower than the perfluoro compound, as might be expected from its structure.

Turning now to the more important factors which influenced these fluorinations, perhaps the most basic of these was the structure of the hydrocarbon being fluorinated. As the molecular weight of the latter increased, the reactivity of the intermediates decreased, due to the close crowding of fluorine atoms, so that increasingly powerful operating conditions were required to attain the perfluoro compound. This necessarily increased the likelihood of combustion and cleavage, which had to be compensated by other means. Also, when the nature of the sample permitted the formation of many structural isomers, or else allowed easy

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[4] Paper XIX, THIS JOURNAL, **77**, 3007 (1955).

[5] R. D. Dresdner, *ibid.*, **78**, 878 (1956).

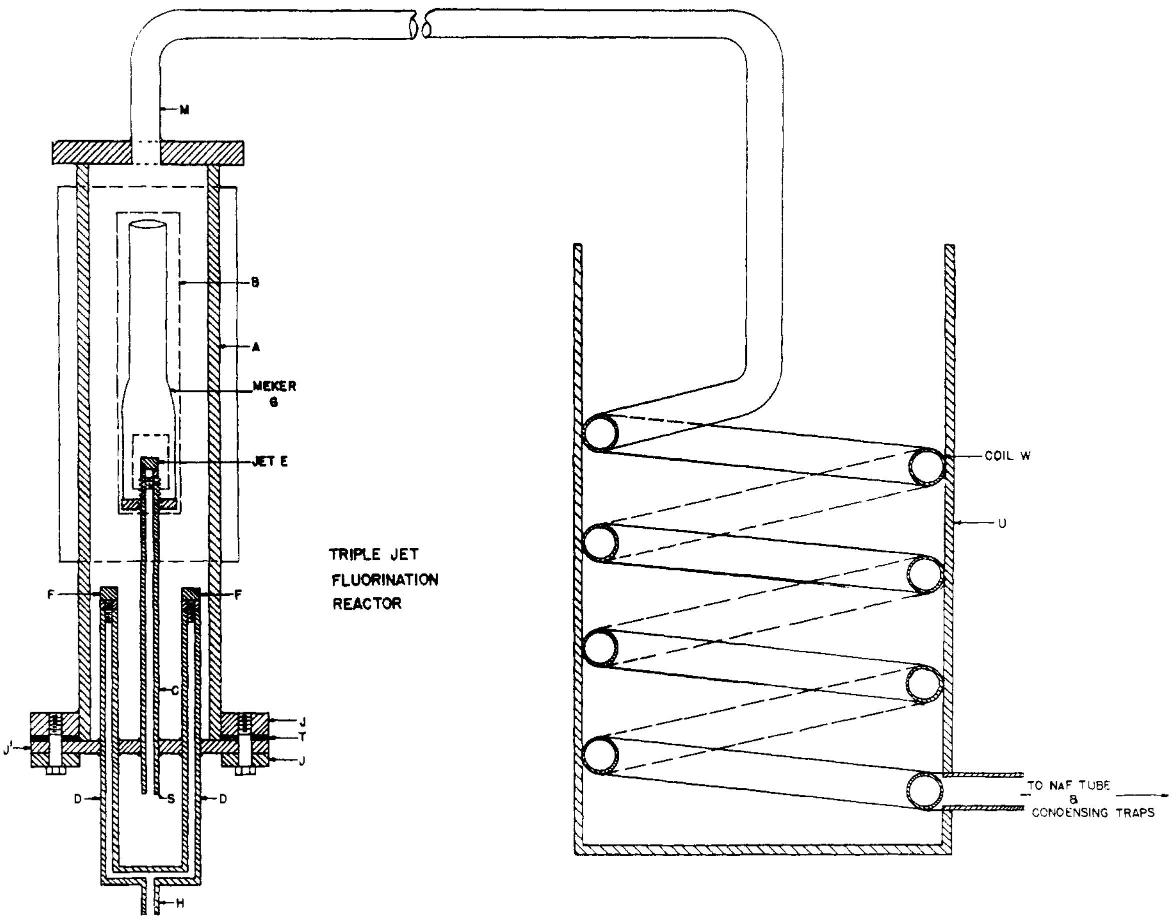

Fig. 1.

dehydrofluorination with the production of additional unsaturated geometric isomers, as in the case of *n*-butane, the fluorinated products tended to become complex and sometimes could not be resolved effectively. Finally, as in the case of neopentane, where the products were largely subliming solids, special equipment for high pressure fractionation was required, as described earlier.

The most powerful operating factor was clearly the molar fluorination ratio (F_2:sample), which could be used in general to direct the fluorination toward any desired level, largely but not entirely without reference to the other operating conditions involved, as illustrated in Table II, runs 1, 2, 3 and 12. However, when this ratio was too high, combustion and cleavage were in general increased, and when it was too low, much undesirable polymerization resulted (run 12).

Of the other factors, perhaps the dilution ratio (F_2:diluent) was the most important on account of its varied effects. An increase in this ratio not only increased the jet pump action and turbulence, which were essential for the dissipation of heat, but also reduced the pass time for the reactants through the several reaction zones, all of which tended to reduce the vigor of the fluorinations involved up to a certain point. Beyond this, however, the overall back pressure in the system gradually rose, which again increased the vigor of the fluorination (Table II, runs 3, 6, 7 and 8), due to a molecular crowding effect leading ultimately to cleavage and periodic combustion, mostly in the secondary reactor, accompanied by violent fluctuations in pressure in the system. These effects were obviously opposed to each other and required careful regulation. It should also be noted that at high fluorination ratios too low a dilution likewise induced combustion (note 1).

The sample flow rate was also of considerable significance, since, other factors being constant, it controlled directly the quantity of reactants present in the system at any one time, the total heat which had to be dissipated to avoid combustion, and the pass time previously referred to as well. In addition, this factor determined the overall yield per hour of operating time, and experience has shown that for mild fluorinations in general the lowest sample flow rate consistent with a reasonable operating time was most effective.

The temperatures of the primary and secondary reactors were of course important, but they were not nearly as critical as might have been expected. The temperature of the primary reactor when equipped with a Kel-F window could not be raised much above 120°, but this maximum was distinctly advantageous (Table II, runs 13 and 16). On the other hand, too low a temperature resulted in sample accumulation and periodic combustion (note 2). The secondary reactor in which the fluorinations were usually completed often had to

TABLE II

THE JET FLUORINATION OF ISOBUTANE UNDER PROGRESSIVELY VARYING CONDITIONS

Results expressed in liquid vol. % of total crude; sample flow rate 0.03 mole/hr.; operating time 5.5–6 hr.

Run	Fluorn. ratio	Diln. ratio	Temp., °C.		Crude, cc.	Cleavage	$(CF_3)_3CF$	C_4HF_9	$C_4H_2F_8$	$C_4H_3F_7$	Residue
			Prim.	Sec.							
1	11:1	1:10	100	250	18	12	88	..	..	..	..
2	10:1	1:10	100	250	18	9	70	22	..	..	..
3	9:1	1:10	100	250	18	5	36	24	..	..	30[a]
4	10:1	1:12	100	250	16	12.5	75	12.5	..	..	..
5	10:1	1:14	100	250	15.5	10	71	19	..	..	..
6	9:1	1:12	100	250	18	11	28	39	..	..	22[a]
7	9:1	1:14	100	250	15	11	26	41	..	..	22[a]
8	9:1	1:16	100	250	17	15	19	34	..	..	31[a]
9	8:1	1:14	100	250	15.5	10	10	23	23	..	36
10	8:1	1:16	100	250	14.5	11.5	11.5	23	23	..	33
11	8:1	1:12	100	250	16	9.5	13	26	27	..	26
12	8:1	1:10	100	250	15.5	13	7	27	27	..	27
13	9:1	1:12	100	175	15	3	26	36.5	26	..	10
14	9:1	1:12	100	100	15	3.5	20	33	32	..	12
15	9:1	1:12	100	40	15	7.5	11.5	28	30	..	23
16	9:1	1:12	120	175	15.5	3	32	39	18	..	8
17	7:1	1:16	120	100	15	9		14.5	33	22	22
18	6:1	1:18	120	100	15	6.5		20	21	33	20
19	7:1	1:16	120	175	15	6		35	35	12	12

[a] Combined dihydro, trihydro and residue. Notes: (1) A run at 10:1 and 1:8, with temperatures 100° and 250°, gave periodic combustion with pressure fluctuations due to the low dilution. (2) A run at 9:1 and 1:12 with temperatures 80° and 175°, gave periodic combustion and pressure fluctuations due to too low a temperature in the primary reactor. (3) Three other runs at fluorination ratios of 0.5:1, 1:1 and 2:1, and otherwise very mild conditions, returned only varying amounts of unreacted sample and polymeric residue.

be raised to 250° or higher when best yields of a perfluorinated product were desired (run 1) on account of the generally mild nature of jet fluorinations, but at lower fluorination ratios when partially fluorinated products accumulated, lower temperatures sometimes resulted in increased cleavage, perhaps due to combustion (runs 13, 14 and 15). On the other hand, when the triple jet reactor was employed to obtain partially or slightly fluorinated products of low molecular weight, coil temperatures as low as 0° have been used effectively (Table III). In all cases, however, the temperature of the respective unit must be kept high enough to avoid premature condensation of any component of the reaction mixture, since a liquid condensate would be likely to enter into immediate combustion with the fluorine.

Finally, the type of reactor to be used in a given fluorination remains to be considered. The single jet system previously described,[4] now using a $^1/_{32}$ inch jet to avoid back pressure and a 1.5-inch coupling between the primary and secondary reactors, was used successfully for the preparation of nearly all of the polyfluoro compounds studied. However, when only one or two atoms of fluorine per mole of hydrocarbon were to be introduced, the new triple jet reactor described below, in which both sample and fluorine were introduced through $^1/_{32}$ inch jets and the products passed rapidly into a long copper coil at a controlled temperature, was very effective.

From the preceding observations it is clear that, while the various factors which have been discussed are often interdependent, a distinct advance has been made in the orientation of simple direct fluorinations in the direction of desired products in adequate yields by properly controlling the operating conditions, and making use of a convenient continuous jet process, which could readily be adapted to large scale production as a future development.

Experimental

Apparatus.—The original jet fluorination system has been illustrated and described in detail in an earlier paper.[4] In general, it consisted of vertical electrically heated brass primary and secondary reactors, placed side by side, and connected at the top by copper tubing. The former contained the jet unit mentioned in the introduction above, and carried a small observation window opposite the jet, while the latter in which the reactions were completed was otherwise empty. In a first modification used in the earlier stages of this work the primary reactor was equipped with a large additional rectangular Kel-F window, through which the entire reaction chamber could be viewed; and the jet unit was especially designed so that it could be readily disassembled for cleaning and repair. Later it was found more convenient to place the secondary reactor vertically above the primary unit, being connected to it by a 1.5″ metal coupling; and still later the windows were omitted since the blue cold flame, previously described, did not appear during the fluorination of samples of higher molecular weight. It has also been found better to use $^1/_{32}$″ jets to avoid significant back pressures at high dilutions.

For very mild fluorinations intended to introduce only one or two atoms of fluorine per mole of sample, a new triple jet reactor has been designed and used, which is illustrated to scale in Fig. 1, and will now be described in detail. The reactor body A was an insulated brass pipe, 2.5″ i.d. × 12″ long, closed at the top by a brass plate welded on, and equipped with a fitting below M and connecting to the copper coil W in which reactions were completed. The reactor was provided with a large Kel-F window 6.25″ × 1″, and an iron ring J welded on at the bottom. Then a brass ring J′, carrying the jet assembly and provided with Teflon gasket T, was inserted and covered with a second iron ring J; after which the whole was securely bolted together as shown in the figure. The inner assembly consisted of the usual turbulent $^1/_{32}$″ sample jet E, surrounded by the Meker tube G which now extended almost to the top of the unit. There were also two steel $^1/_{32}$″ fluorine jets F, F, carried on brass tubing and placed below and to each side of the Meker tube as shown in the figure. The coil W, previously referred to, was made from 20′ of 0.625″ copper tubing attached to the reactor at

TABLE III

OPERATING CONDITIONS CORRESPONDING TO MAXIMUM YIELDS AS GIVEN IN TABLE I

Highly fluorinated

Product	Reactor type	Sample flow rate	Fluorn. ratio	Diln. ratio	Temp., °C.		Operat. time, hr.	Crude, cc.
					Prim.	Sec.		
C_2F_6	Single	0.03	7:1	1:10	100	175	8	11
C_3F_8	Single	.02	9:1	1:11	100	175	7	10
n-C_4F_{10}	Single[a]	.02	11:1	1:10	120	245	7	16
$(CF_3)_3CF$	Single	.03	11:1	1:10	100	250	6	18
CF_3CHF_2	Single	.06	4:1	1:6.7	70	79	3	10
$C_2F_6CHF_2$	Single	.03	7:1	1:10	40	35	6	12
$(CF_3)_2CFCHF_2$	Single	.03	9:1	1:14	100	250	5.5	15
$(CF_3)_3CCHF_2$	Single	.03	13.1	1:10	120	250	4	14
$C_3H_2F_6$	Single	.03	6:1	1:11.5	40	35	6	12
$C_4H_2F_8$	Single	.03	7:1	1:16	120	175	5.5	15
$C_5H_2F_{10}$	Single	.01	15:1	1:15	120	250	12	14
Partially fluorinated								
CHF_2CH_2F	Triple	0.06	3:1	1:21	Coil	30	8	16
CH_2F_2	Triple	.05	1.5:1	1:53	Coil	0	8	4
CH_3CHF_2	Single	.06	0.5:1	1:133	30	0	5	6
CH_3F	Triple	.1	0.5:1	1:80	Coil	0	6	4.5
CH_3CH_2F	Triple	.06	0.5:1	1:127	Coil	0	10	24
$C_2H_5CH_2F$	Triple	.06	2:1	1:29.2	Coil	0	9	17

[a] 1/16" jet used in this case.

M, and contained in the metal can U. The lower end extended through the bottom of the can to be connected to the collection system.

In operation, metered fluorine diluted with metered helium was introduced through H and jets F, while metered sample, also diluted with helium came in through S and the jet E. When the jet velocity exceeded the flame velocity, the highly turbulent, well-mixed and reacting gases passed rapidly and without flame directly into the coil W, which was maintained at a definite temperature and in which the fluorination was gradually completed. In all cases the products were passed over sodium fluoride pellets, usually at 100° to remove hydrogen fluoride, condensed in refrigerated traps, and precision rectified in the usual manner.

Very nearly pure fluorine was supplied at first from Harshaw electrolytic cells as previously described, and later from commercial cylinders provided with complete safety equipment, as furnished and recommended by the General Chemical Co. This fluorine gas was rated at better than 99% pure, and was measured by means of calibrated rotameters. The hydrocarbon samples were taken directly from commercial cylinders supplied by the Mathieson Co. and were rated from 95 to 99.9% pure.

Fluorinations.—In this broad study some 120 runs have been completed over a period of nearly four years, and it is obviously not possible to present all the data in full detail here. Consequently, the representative material dealing with the fluorination of isobutane will be given (Table II), followed by a listing of the experimental conditions (Table III) corresponding to the optimum yields obtained in the whole study as presented in Table I in the Discussion section.

A typical procedure for the fluorination of isobutane, which is illustrative of the operation used throughout, follows: Isobutane was passed directly from the commercial cylinder through a calibrated flowmeter at the rate of 0.03 mole/hour into the lower section of the primary reactor, where it was diluted with metered helium at the rate of 3.24 moles/hour. The diluted sample then passed through the highly turbulent jet, and met undiluted fluorine, rising around the jet at the rate of 0.27 mole/hour, and simultaneously diluted with reactor gases, maintained at 120°, being recycled by jet pump action. Under these conditions the molar fluorination ratio (F_2:sample) was 9:1, the dilution ratio (F_2:He) 1:12, and the reaction ratio therefore 9:1:108. The reaction was completed in the secondary reactor, which was maintained at 175°, and the exit gases were then passed through a pipe packed loosely with NaF pellets at a temperature of 100° to remove the hydrogen fluoride generated in the reaction. After 5.5 hours of operation, 15.5 cc. of crude product had collected in the refrigerated glass traps, and was then rectified without stabilization in the Booth-Podbielniak low temperature still.

The results will be found as run 16, Table II, in which are collected the products obtained by the fluorination of isobutane under all conditions studied. The yields are expressed as liquid volume percentages of the total crude condensate in each case. Transition fractions were incorporated equally into the fore and after cuts unless they exceeded 4–5%, in which case they were collected separately.