FLUOROINDENES.

11.* RADICAL ROUTE FOR THE REACTION OF PERFLUORINATED 3-METHYLINDENE, 1-METHYLENEINDANE, AND 1-ETHYLIDENEINDANE WITH NITRIC ACID

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The reaction of N_2O_4 , and also HNO_3 purified from oxides of nitrogen, with perfluoro-3-methylindene and perfluoro-1-methyleneindane takes place at the multiple bond of these compounds and results, after hydrolysis, in mixtures, of similar composition, of the corresponding nitro-1-hydroxy and dinitro derivatives. In contrast, whereas perfluoroindene and HNO_3 do not form perfluoro-1,2-dinitroindane, the latter is formed from N_2O_4 . Furthermore, perfluoroindene reacts with HNO_3 in acetic acid in the presence of CF_3SO_3H , but there is no reaction in its absence. From these results one can apparently assume that the reaction of perfluoro-3-methylindene and perfluoro-1-methyleneindene with HNO_3 proceeds by a radical route, but that of perfluoroindene with HNO_3 is electrophilic.

The reaction of polyfluorinated aromatic compounds [2] and polyfluoroolefins [3, 4] with nitrating reagents has been studied in some detail. These transformations are of theoretical interest and they also open up wide synthetic possibilities [2-4]. Among similar reactions of polyfluorinated indenes, only the nitration of perfluoroindene (I) [5] and perfluoro-2-methylindene [6] has been studied. In this connection, to develop an overall mechanism for the reaction of polyfluoroindenes with nitrating agents and to clarify their synthetic possibilities, in the present work we have studied the reaction of indene (I), 3-chlorohepta-fluoroindene (II), perfluoro-3-methylindene (III), perfluoro-1-methyleneindane (IV), and perfluoro-1-ethylindane (V) with nitric acid and with N_2O_4 .

It has been shown that in the reaction of methylindene (III) with nitric acid, free from oxides of nitrogen, in addition to r-l-hydroxy-t-2-nitroperfluoro-l-methylindane (VI) one obtains cis-(VIII)- and trans-1,2-dinitroperfluoro-l-methylindanes (VIII). Compound (IX), r-l-hedroxy-c-2-nitroperfluoro-l-methylindane, isomeric with compound (VI), is not detected in this case. At the same time, compound (IX), which is formed by heating (VI) in the presence of silica gel, is not changed by the action of HNO₃ (see top of following page).

It would seem that the formation of compounds (VII) and (VIII) can be taken as evidence of a radical mechanism for the reaction of methylindene (III) with HNO_3 . This assumption is not contradicted by the result of the reaction of (III) with HNO_3 in sulfuric acid, leading to the products (VI) to (VIII). The rate of the process in this case is considerably lower than in nitric acid. The reduction in the rate could be the result of both partial suppression of the radical reaction and the heterogeneous nature of the reaction in nitration mixture.

In this connection, we studied the reaction of methylindene (III) with the radical nitrating agent N_2O_4 . It was shown that, in this reaction, at 20°C, in addition to the dinitro derivatives (VII) and (VIII), r-2-nitroperfluoro-c-1-methylindanyl-1-nitrite (X) is formed. Treatment of this mixture with water yielded products (VI)-(VIII) in approximately the same

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ratio as in the reaction with HNO_3 . A mixture of compounds (VII), (VIII), and (X) prepared at 20°C was converted at 70°C into a mixture of (VII) and (X), heating of which at 120°C resulted in the formation of product (X) alone. It should be noted that the dinitro derivative (VIII) is gradually isomerized to (X) at room temperature also.

Addition of two nitro groups at the double bond of the substrate is also observed in the reaction of methyleneindane (IV) with nitric acid or N_2O_4 . In the first case, in addition to 1-nitroperfluoro-1-nitromethylindane (XI), an approximately equal quantity of 1-hydroxyperfluoro-1-nitromethylindane (XII) is also formed. In the reaction of (IV) with N_2O_4 there is rather more of the dinitroderivative (XI) in the reaction mixture than of perfluoro-1nitromethylindanyl-1-nitrite (XIII). After treatment of this mixture with water the ratio of the alcohol (XII), formed from the nitrite (XIII), and the dinitroindane (XI) coincides with that of (XIII) and (XI) in the original mixture. At 70°C the dinitroindane (XI) is completely converted into the nitroitrite (XIII).



The formation of the dinitro derivative (XI) in the reaction of (IV) with HNO_3 can apparently be taken as evidence for a radical mechanism for the process. This is not contradicted by the observed slowing of the reaction of (IV) with HNO_3 in sulfuric acid, leading to the products (XI) and (XII). The reduction of the reaction rate in nitration mixture in comparison with HNO_3 can be explained in a similar way to the analogous conversion of methyl-indene (III).

In contrast to compounds (III) and (IV), ethylideneindane (V) (ratio of isomers E:Z \approx 2:1) does not react with nitric acid at room temperature; at 55°C it gives 1-hydroxyper-fluoro-1-(1-nitroethyl)indane (XIV) in the form of a mixture of two diastereomers in 3:1 ratio. Diastereomers of perfluoro-1-(1-nitroethyl)indanyl-1-nitrite (XV) are obtained in the same ratio by the action of N₂O₄ on (V) at 55°C and likewise for the diasteromers of the alcohol (XIV) formed by the hydrolysis of this nitrite.



In the reaction of (V) with HNO₃ or N₂O₄ at 55° no l-nitroperfluoro-l-(l-nitroethyl)indane (XVI) is detected. The absence of (XVI) is apparently the result of its instability at the reaction temperature. In fact, on reacting (V) with N₂O₄ under mild conditions (~20°C, 20 h) a mixture is obtained which apparently contains the dinitro derivative (XVI) (from the ¹⁹F NMR spectrum of the mixture) in addition to the initial (V) and the nitronitrite (XV). On prolonged standing (6 days) or at 55°C this mixture is converted to the nitronitrite (XV). Results for the thermal stability of the dinitroderivatives (VII), (VIII), and (XI) are not at variance with this hypothesis.

It should be noted that the nitroalcohol (XIV) which is stable in acid media is converted in the presence of K_2CO_3 or on a column of silica gel into the perfluoroindanone-1 (XVII). The reaction apparently proceeds by a type of haloform dissociation via an intermediate anion which is formed by deprotonation of the alcohol (XIV).

The electrophilic addition of nitrating agents to octafluoronaphthalene [2, 7], on the one hand, and the possibility of a radical route for the reaction of compounds (III)-(V) with HNO₃ on the other, prompted us to examine the reaction of the indene (I) with HNO₃ and N_2O_4 . It was shown that 2-nitroperfluoroindanone-1 (XVIII) is obtained when (I) is dissolved in HNO₃ at 20°C. Detection of 1,2-dinitroperfluoroindane (XIX) was not achieved. The latter is formed as a mixture of cis- and trans-isomers, in addition to the ketone (XVIII), in the reaction of indene (I) with N_2O_4 . It was shown by separate experiments that the dinitroindane (XIX) is not changed under the conditions of the reaction of indene (I) with HNO₃, nor at 120°C in the absence of HNO₃ (see top of following page).

The results obtained seem to show that the reaction of indene (I) with HNO_3 , in contrast to compounds (III)-(V), proceeds not by a radical but by an electrophilic mechanism. The reaction of indene (I) with a mixture of nitric and acetic acids with and without the addition of CF_3SO_3H [7] is in accord with this view. In fact, the reaction does not proceed in the absence of CF_3SO_3H while in its presence one obtains a mixture of the cis- and trans-isomers of (2-nitroperfluoroindanyl-1)trifluoromethylsulfonate (XX). In the latter case the reaction



goes quite slowly and one can observe the separation of the mixture into layers as it proceeds. The individual product (XX) is prepared by the reaction of indene (I) with HNO_3 in CF_3SO_3H .

Sulfuric acid acts on the sulfonate (XX), converting it into the indanone (XVIII). The structure of the latter is supported by its synthesis from indene (II) and HNO_3 . It should be noted that in reaction with methanol the indanone (XVIII) undergoes a haloform type of dissociation [8] as a result of which methyl 2-(1,1,2-trifluoro-2-nitroethyl)tetrafluoro-benzoate (XXI) is formed. The action of water on ketone (XVIII), or dilution of its solution in HNO_3 with water, gives hexafluorohomophthalic acid (XXIII) in addition to 2-(1,1,2-trifluoro-2-nitroethyl)tetrafluorobenzoic acid (XXII); (XXIII) does not appear to be a product of the conversion of (XXII). In these circumstances, the ketone (XVIII) was isolated from the reaction mixture after dilution with concentrated sulfuric acid.

The difference in the behavior of compounds (I) and (III)-(V) with HNO_3 can apparently be explained by the relative stability of the benzyl type cations and radicals corresponding to the addition of NO_2^+ or NO_2^- to (I) or to (III)-(V), for example



In fact, on account of the presence of the CF_3 acceptor group, the cation (IIIa) must be less stable than (Ia) [9], while the radical (IIIb) must be more stable than (Ib) [4, 10], i.e., on passing from (I) to (III) the probability of an electrophilic process must decrease, and of a radical process increase.

The configuration of compounds (VI)-(X) was assigned on the basis of an analysis of the fine structure of the signals from the CF₃ group in the ¹⁹F NMR spectra of these compounds. In all cases, $J_{CF_3-F^7}$ amounted to 14-20 Hz. The value of $J_{CF_3-F^2}$ depended on the structure of the product. It was assumed that it was greater when the interacting nuclei were situated on one side of the plane of the five-membered ring than when they were on opposite sides (cf. [11]). In compounds (VII) and (IX), $J_{CF_3-F^2}$ amounted to 20 and 18 Hz, respectively, and in compounds (VI), (VIII), and (X), to <5 Hz. The observed spin-spin coupling constants are found to be in accordance with those for the cis- and trans-isomers of 1,2-di-bromoperfluoro-1-methylindane [1].

o, ppma Com- \mathbf{F}^{i} F3 $J_{\mathbf{A'B'}}(J_{\mathbf{AB}}),$ pound CF₃ (CF₂NO₂) F4 F'5,6 $\mathbf{F}^{\mathbf{7}}$ (OH)(Hz) A в B A' (VI) 23,617.0; 19.0 26.989.8 (4,2)18,1 26071,9 22.9: 21,9 38,4 22,3: 21,4 32,1 (VII)b 24,6 70,5 72,0 94.3 22,7 58,2 260(VIII) 25.398,8 28,4 51,8 261**17.8:** 19,8 **24,3** 17,6: 19,1 **28**,7 **22,3:** 21,2 **34**,8 24.3 (IX) 70,3 72,2 86,1 (4,2)15,5 26358,0 23,9 25,2 (X) 51,8 93,6 20,0 259 (XI) 44,4 36,4 (78, 6)49,8 57.7 (250)23,8 (XII) 17,4: 18,9 27,3 41,4 59,0 . 54,6 (70, 6)(4, 4)265 (249) 24,6 24,4 (XIII) (XIV) Þ 59,8 63,7 53,3 50,7 18,2: 19.0 29,4 (70,5)44,9 38,8 262 (246) 18,5: 19,2 30,3 87,8; (4,9)44,3 37,3 264 (241) 28,1C 24,8 18,5; 19,7 27.5 or 90,7; 44,9 38,0 (4,9)262 (243) 61,1 52,430,0 30,0 or 27,5 C 28,3: 20,9 23,5; 22,1 24,2: 22,5 22,4: 21,4 22,5: 22 (XVIII) 27.031,5 65,3 70,2 68,8 72,4 73,9 26820.353,4 26,3 25,9 25,6 26,8 (XIX) b 19,8 25,9 23,3 33,7 58,226231,7 27,5 47,8 58,8 260(XX)88,7 89,5 50,5 53,9 26225.9 25,9 69.9 21.5 53.8 260

TABLE 1. ¹⁹F and ¹H NMR Spectra of Polyfluoroindanes

a) Spectra were run in solution in CCl_4 , concentration 11 mole %. Chemical shifts are downfield from C_6F_6 and TMS. C_6F_6 or HMDS (0.04 ppm from TMS) were used as internal standards. For compounds (XIV), (XIX), and (XX) the first result given is for the isomer formed in greater quantity. b)¹⁹F NMR spectra run on a Bruker WP 200 SY for solutions in CDCl₃. c) $-CF(NO_2)-$.

EXPERIMENTAL

Fluorine-19 and proton NMR spectra were run on a Varian A-56/60A instrument using the reaction mixtures without solvent and solutions of the compounds in CCl_4 . The UV spectra were obtained on a Specord UV-VIS spectrophotometer in heptane. Nitric acid was purified by the method of [12]. Nitrogen dioxide was prepared by the method of [13]. The results of the ¹⁹F NMR spectra of the polyfluoroindanes are shown in Table 1, and the results of elemental composition determinations and IR and UV spectra are given in Table 2.

<u>2-Nitroperfluoroindanone-1 (XVIII).</u> a) To 2.2 g HNO₃ stirred at 0°C was added, dropwise, 1 g (I) and the prepared solution kept at 0°C for 5 min and at 20°C for 0.5 h. It was then treated with concentrated H_2SO_4 , extracted with CH_2Cl_2 , and the solvent distilled off. Distillation in vacuum (70°C/5 mm) yielded 1.15 g (XVIII), mp 57-60°C. After recrystallization from CH_2Cl_2 -hexane and subsequent distillation in vacuum, mp 61-62°C.

b) To 0.55 g HNO_3 stirred at 0°C was added 0.1 g (II), the mixture kept 1 h at 20°C, treated with concentrated H_2SO_4 , extracted with CH₂Cl₂, and the solvent distilled off. Distillation in vacuum (70°C/5 mm) gave 0.1 g (XVIII), mp 57-60°C.

<u>Reaction of (XVIII) with Water.</u> a) A solution of 1.57 g (XVIII) in 5 ml CHCl₃ was stirred with 10 ml water for 1.5 h at 20°C. It was extracted with CHCl₃ and then with ether and the extracts dried over MgSO₄. After distilling off the solvent from the extracts there was obtained, respectively, 0.83 g (XXII), mp 87-89°C, and 0.60 g (XXIII) the IR and ¹⁹F NMR spectra of which coincided with those of an authentic sample [14]. Compound (XXII). PMR spectrum (δ , ppm): 11.0 (COOH), 6.3 (CFH), JgemHF = 47, Jvic HF = 8 Hz. ¹⁹F NMR spectrum (δ ppm from C₆F₆): 58.7 (CF₂), 28.1 (F³), 25.6 (F⁶), 16.9 (F⁵), 14.0 (F⁴), 3.7 (CFH), J_{CF₂-F³FF = 29, J_{CFH}-F³FF = 9, J_{CF₂}-CFH^{FF} = 13 Hz.}

b) A reaction of 1 g (I) and 3 g HNO_3 was carried out as described above, the mixture poured into water, extracted with ether, dried over $MgSO_4$, and the solvent distilled off. Yield 1.05 g of a mixture of (XXII) and (XXIII) (2:1 by ¹⁹F NMR spectrum).

(UV spectrum À _{max} , nm (lg E)			269(3,01)	272(3,30)	276(3,11)			273(3,15)	268(3,05)			249(4,00), 256(4,05) 290(3,23), 296(3,23)	273(3,02)	273(3,04)	272 (3,10)	275 (3,36)	274(3,11) c
, (XVIII)-(XXII	, cm ⁻¹		other bands	3544; 3251(OH); 1420	1416	1422	3565, 3259(OH); 1411	1£11, 1732(ONO), 1412	1414	3521, 3267(OH), 1416	1810, 1732(ONO), 1403	3500(OH) 1410	1774(C=0) 1632, 1400	1424	1454, 1421	1453, 1416	3017, 2964(C-H), 1762, 1743(C=O),	2500- 1743 2500- 3300 (OH), 1728 (C=0) 1633, 1/23
(VI)-(XIV)	R spectrum, V		—N02 asymm.a	1603	1622, 1606	1617, 1610	1605	1601	1609	1603	1600	1605	1600	1618	1612	1608	1598	1596
f Compounds	Π	fluorinated	aromatic ring	1522	1530	1531	1522	1523	1525	1516	1522	1516	1517	1532	1532	1527	1487	1485
l IR Spectra o		Empirical	tormula	C ₄₀ HF ₄₀ NO ₃		C ₁₀ F ₁₀ N ₂ O ₄	C ₁₀ IIF ₁₀ NO ₃	C ₁₀ F ₁₀ N ₂ O ₄	C10F10N2O4	C10HF10NO3	C ₁₀ F ₁₀ N ₂ O ₄	C ₁₁ HF ₁₂ NO ₃	C ₉ F7NO 3	$C_9F_8N_2O_4$	$C_{10}F_{11}NO_5S$	C ₁₀ F ₁₁ NO ₅ S	C ₁₀ H4F7NO4	C ₉ H ₂ F ₇ NO,
and UV and			z	3,63 3.75	5	7,05	3,43 $3,75$	6,97 6.97	7,29	3,60	7,10 6.97	3,54 3,31	4,60	7,71 7,71	2,51	3,10 3,10		4,23
Analysis	culated, %		f±4	51,30 50 00	1000	47,33	50,60	47,20	47,12	50,60 50,92	47,32	53,65	43,60 43,88	43,13 43,13	45,83 25 00	45,87 45,92 45,92		41,24
mental /	Found/Cal		(S) II	0,44	1710		0,23			0,32		$\frac{0,27}{0.24}$	1		$\left(\frac{7,22}{7,04}\right)$	(6, 66) $(7, 04)$		0,64 0,63
a for Ele			υ	31,94	01,20	30,19	32,32 32,49	30,18	30,23	31,93 32,49	29,96 29,96	31,15	35,64 35,64	30,76	26,49	26,33 26,39		33,65 33,66
TABLE 2. Data	Compound			(VI)	(111)	(VII) + (VIII) 1:6	(IX) + (VI) 5,6:1	(X)	(IX)	(IIX)	(IIIX)	(XIV)	(IIIAX)	(XIX)	(XX)	(XX) ratio of isomers	1:1 (XXI)	(IIXX)

a) Band of symmetrical stretching vibrations of NO₂ group not identified because of presence of bands due to other groups at same frequency (1300-1360 cm⁻¹). b) Determined by high-resolution mass spectrometry on a Finnegan MAT 8200. c) In C_2H_5OH .

A solution of 0.2 g (XXII) in 1.2 g $\rm HNO_3$ was poured into water, extracted with ether, and dried over MgSO₄. Distilling off the solvent yielded 0.2 g (XXII) having no (XXIII) as impurity (by ¹⁹F NMR).

<u>Methyl 2-(1,1,2-Trifluoro-2-nitroethyl)tetrafluorobenzoate (XXI)</u>. A solution of 0.62 g (XVIII) in 1 ml methanol was kept for 20 h at ~20°C. After distilling off the solvent in vacuum (~20 mm) and distillation in a molecular still (120°C/2 mm), 0.60 g (XXI) was obtained. PMR spectrum (δ , ppm): 6.4 (CFH), 4.0 (CH₃); J^{HF}_{gem}= 48, J^{HF}_{VIC}= 9 Hz. ¹⁹F NMR spectrum (δ , ppm from C₆F₆): 57.7 (CF₂), 27.4 (F³), 24.7 (F[°]), 16.1 (F⁵), 12.6 (F⁴), 3.4 (CFH); J_{CF₂-F³}^{FF} = 28, J_{CFH-F₃}^{FF} = 8, J_{CF₂-CFH}^{FF} = 13 Hz.

Nitration of (I) by Nitric Acid in CF_3SO_3H and in CH_3COOH . a) To 0.40 g HNO_3 in 2.62 g CF_3SO_3H was added 1 g (I), dropwise while stirring at 20°C over a period of 20 min. This was stirred for 20 min, treated with water, extracted with CH_2Cl_2 , dried over $MgSO_4$, and the solvent distilled off. Molecular distillation yielded 1.73 g (XX) (ratio of isomers 5:1 by ¹⁹F NMR). Repeated recrystallization from hexane yielded the pure predominant isomer of (XX), mp 68-69°C, and a mixture of isomers of (XX) in the form of an oily liquid.

A mixture of 0.15 g (XX) and 1.2 g H_2SO_4 was agitated in a sealed ampul for 6 h at 100°C, the solvent distilled off, and the residue distilled (70°C/10 mm) to yield 0.08 g (XVIII) (¹⁹F NMR spectrum), mp 57-60°C.

b) To a mixture of 0.2 g HNO_3 , 0.19 g CH_3COOH , and 0.25 g CF_3SO_3H was added 0.4 g (I) and the mixture kept 12 days at ~20°C. It was poured into water, extracted with CH_2Cl_2 , dried over MgSO₄ and the solvent distilled off. The residue was 0.4 g of a mixture containing (from the ¹⁹F NMR spectrum) 70% (I) and 30% (XX).

c) In a mixture of 0.2 g $\rm HNO_3$ and 0.19 g $\rm CH_3COOH$ was dissolved 0.4 g (I) and the solution kept 12 days at ~20°C. It was poured into water, extracted with $\rm CH_2Cl_2$, dried over MgSO₄, and the solvent distilled off. Yield 0.38 g of starting material (¹⁹F NMR).

Reaction of (I) with N_2O_4 . a) To 0.74 g N_2O_4 , stirred at -10°C, was added, dropwise, 0.70 g indene (I). It was stirred 0.5 h at -10°C, 0.5 h at 20°C. From the ¹⁹F NMR spectrum, the product was (XVIII) and (XIX) in 5:4 ratio. Compound (XIX) was a mixture of geometrical isomers in the ratio 3.5:1. On heating the reaction mixture for 16 h at 120°C in a sealed ampul its ¹⁹F NMR spectrum was unchanged. The mixture was treated with water, extracted with ether, dried over MgSO₄. Distilling of the solvent left 0.84 g residue which was transferred to a column of SiO₂, and eluted therefrom with pentane, CH₂Cl₂, and ether. Distilling off the solvents yielded, respectively, 0.29 g (XIX), 0.20 g (XXII), and 0.18 g (XXIII).

b) A 5:4 mixture of (XVIII) and (XIX) (1 g) was dissolved in 2 g HNO_3 and kept for 0.5 h at 20°C. ¹⁹F NMR showed that the ratio of (XVIII) and (XIX) was unchanged.

<u>Reaction of Compounds (III)-(V) with N₂O₄.</u> a) A mixture of 0.40 g (III) and 0.30 g N₂O₄ was kept in a sealed ampul for 12 h at 20°C. From the ¹⁹F NMR spectrum, the mixture then contained (VII), (VIII), and (X) in the ratio 9:55:36. It was poured into water and the organic layer (0.45 g) dried over MgSO₄. On a column of SiO₂, using pentane as eluent, there was separated 0.23 g of a mixture of (VII) and (VIII). Ether was used to elute 0.13 g (VI) which was further purified by molecular distillation in vacuum (70°C/2 mm).

b) In an experiment similar to the preceding, from 0.40 g (IV) and 0.30 g N_2O_4 there was obtained, after 12 h at 20°C a mixture of (XI) and (XIII) in 1.3:1 ratio (¹⁹F NMR spectrum). This was treated with water and dried over MgSO₄. Elution with pentane on a column of SiO₂ separated 0.26 g (XI) and elution with ether yielded 0.14 g (XII). The latter was purified by molecular distillation in vacuum (70°C/2 mm).

c) A mixture prepared from 0.40 g (III) and 0.30 g N_2O_4 (12 h at 20°C) was kept for 10 h at 70°C in a sealed ampul. From ¹⁹F NMR data it contained (VII) and (X) in 1:9 ratio. After keeping this mixture for 16 h at 120°C the product (X) was obtained (¹⁹F NMR) from which N_2O_4 was additionally distilled in vacuum. Hydrolysis of (X) yielded 0.35 g alcohol (VI).

d) A mixture prepared from 0.40 g (IV) and 0.30 g N_2O_4 (12 h, 20°C) was kept for 10 h at 70°C to yield the product (XIII) (¹⁹F NMR spectrum). Hydrolysis of (XIII) yielded 0.35 g alcohol (XII).

e) 1 g (V) and 0.53 g N₂O₄ kept for 8 h at 55°C gave a product which was apparently, from ¹⁹F NMR, a mixture of the diastereomers of (XV) (3:1). This was poured into water, extracted with CH_2Cl_2 , dried over MgSO₄, and the solvent distilled off. The residue was 1.09 g (XIV), a mixture of diastereomers in 3:1 ratio (¹⁹F NMR) which was purified by molecular distillation in vacuum (70°C/2 mm). A solution of 0.25 g (XIV) in 0.5 ml chloroform was added to 0.5 g 10% K₂CO₃, stirred 1 h at 20°C, treated with water, acidified with 5% HCl, extracted with CH_2Cl_2 , dried over MgSO₄, and the solvent distilled off. The residue was 0.15 g (XVII), the ¹⁹F NMR spectrum of which coincided with that of an authentic sample [15]. After passing 0.98 g (XIV) through a column of SiO₂ (CH_2Cl_2 eluent) and redistillation in vacuum (80°C/25 mm), 0.54 g (XVII) was obtained.

<u>Reaction of (III)-(V) with HNO₃.</u> a) To 1.42 g HNO₃ was added, dropwise with stirring, 0.4 g (III), kept for 24 h at ~20°C, poured into water, extracted with CH_2Cl_2 , dried over MgSO₄, and the solvent distilled off. The residue, 0.39 g, contained (¹⁹F NMR) compounds (III), (VI)-(VIII) (32:25:6:38).

b) Similarly, from 0.40 g (IV) and 1.5 g HNO_3 at ~20°C (6 h), 0.41 g of a mixture of (IV), (XI), and (XII) (20:40:40) was obtained.

c) 1 g (III) and 1.4 g HNO_3 stirred 20 h at 40-42°C, and treated as in the preceding experiment. There was 1.14 g of a mixture of (VI)-(VIII) (62:14:24) obtained.

d) To 0.25 g HNO₃ in 1.9 g H_2SO_4 was added 0.40 g (III), stirred 24 h at 40-45°C, poured into water, extracted with CH_2Cl_2 , dried over $MgSO_4$, and the solvent distilled off to yield 0.40 g of a mixture of (III), (VI)-(VIII) (77:14:3:6) (¹⁹F NMR spectrum).

e) To 0.25 g HNO_3 in 2 g H_2SO_4 was added 0.40 g (IV), kept for 200 h at ~20°C, 76 h of this with stirring. Treated as in preceding experiment to yield 0.41 g of a mixture of (IV), (XI), and (XII) (69:8:23) (¹⁹F NMR spectrum).

f) A solution of 1 g (V) in 3.5 g HNO_3 was kept in a sealed ampul for 30 h at 55°C, poured into water, extracted with CH_2Cl_2 , dried over MgSO_4 , and the solvent distilled off; 0.98 g (XVI) was obtained; its ¹⁹F NMR spectrum showed it to be a mixture of diastereomers in the same ratio as in the reaction of (V) with N_2O_4 .

<u>r-l-Hydroxy-c-2-nitroperfluoro-l-methylindane (IX)</u>. A solution of 0.75 g (VI) in 2 ml CCl₄ was heated in a sealed ampul with l g SiO₂ for 6 h at 60°C, eluted with CH_2Cl_2 , and the solvent distilled off. The residue was a mixture (0.68 g) of (VI) and (IX) in the ratio 1:5.6, which was further purified by molecular distillation in vacuum (70°C/2 mm).

LITERATURE CITED

- 1. I. P. Chuikov, V. M. Karpov, V. E. Platonov, and G. G. Yakobson, Izv. Akad. Nauk SSSR, Ser. Khim., 1839 (1988).
- V. D. Shteingarts and G. G. Yakobson, Zh. Vses. Khim. Ova, <u>15</u>, 72 (1970); V. D. Shteingarts, Problems in Physical Organic Chemistry [in Russian], Izd. Leningrad. Gos. Univ. (1984), p. 112.
- 3. B. L. Dyatkin, E. P. Mochalina, and I. L. Knunyants, Usp. Khim., <u>35</u>, 979 (1966).
- 4. B. L. Dyatkin and I. L. Knunyants, Zh. Vses. Khim. Ova, <u>15</u>, 5 (1970).
- 5. V. M. Karpov, V. E. Platonov, and G. G. Yakobson, Zh. Org. Khim., <u>10</u>, 663 (1974).
- 6. V. M. Karpov, V. E. Platonov, and G. G. Yakobson, Izv. Akad. Nauk SSSR, Ser. Khim., 2295 (1976).
- V. D. Shteingarts, O. I. Osina, G. G. Yakobson, and N. N. Vorozhtov, Jr., Zh. Vses. Khim. Ova, <u>11</u>, 115 (1966).
- I. L. Knunyants, A. V. Fokin, and V. A. Komarov, Izv. Akad. Nauk SSSR, Ser. Khim., 466 (1966); T. N. Gerasimova and E. P. Fokin, Usp. Khim., <u>49</u>, 1057 (1980).
- 9. Yu. V. Pozdnyakovich and V. D. Shteingarts, J. Fluor. Chem., 4, 283, 297 (1974).
- B. L. Tumankii, N. N. Bubnov, V. R. Polishchuk, and S. P. Solodovnikov, Izv. Akad. Nauk SSSR, Ser. Khim., 2222 (1981).
- 11. S. Ng and C. H. Sederholm, J. Chem. Phys., <u>40</u>, 2090 (1964).
- G. Brauer (ed.), Handbook of Preparative Inorganic Chemistry, 2nd edn., Academic Press, New York (1963).
- F. M. Rapoport and A. A. Il'inskaya, Laboratory Methods for the Preparation of Pure Gases [in Russian], Goskhimizdat, Moscow (1963), p. 197.
- 14. V. M. Karpov, V. E. Platonov, and G. G. Yakobson, Izv. Sib. Otd., Akad. Nauk SSSR, Ser. Khim. Nauk, Part 2, No. 4, 124 (1974).
- V. M. Karpov, L. S. Klimenko, V. E. Platonov, and G. G. Yakobson, Zh. Org. Khim., <u>11</u>, 2372 (1975).