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# Fluoro-indenes. Part 14*. Interaction of perfluorinated 3-methyl-indene and 1-methylene-indan with nitrating agents in anhydrous HF

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## Abstract

The reaction of perfluorinated 3-methyl-indene and 1-methylene-indan with nitrating agents in anhydrous HF leads to the formation of perfluoro-indan containing an oxygen function together with nitrofluorination products. From an analysis of the experimental data and the results of MNDO calculations of the starting compounds (including perfluorinated indene and 2-methyl-indene), their radical cations and polyfluorinated nitro-indanyl cations, a scheme for the process has been suggested including both a classical electrophilic route and a route involving radical cations of the substrates. The latter are assumed to be generated together with $NO_2\cdot$ from the intermediate nitro-indanyl cations.

## Introduction

The reaction of perfluorinated indene (**1**), 3-methyl-indene (**2**), 1-methylene-indan (**3**) and 1-ethylidene-indan (**4**) with $HNO_3$ [2] and with the $H_2O_2/HF/SbF_5$ system [1] is known to occur at a substrate double bond. The reaction with $H_2O_2/HF/SbF_5$ seems to occur via an electrophilic mechanism [1], whereas with $HNO_3$ this mechanism is only realised in the case of olefin **1**. In all other cases, the reaction proceeds via a radical mechanism [2]. With the aim of further investigating the interaction of compounds **2**–**4** with nitrating agents, we have studied their transformations in $HNO_3/HF$ [3], $HNO_3/SbF_5/HF$ and $NO_2BF_4/HF$ [4]. The nitrofluorination of indene **1** with $HNO_3/HF$ to give 2-nitro-perfluoro-indan has been described earlier [5].

## Experimental

$^{19}F$ and $^{1}H$ NMR spectra were recorded for $CCl_4$ or $CDCl_3$ solutions on Varian A-56/60A (56.4 and 60 MHz) and Bruker AC-200 (188.3 and 200 MHz) instruments. Chemical shifts are given downfield from $C_6F_6$ and TMS; $C_6F_6$ and HMDS (0.04 ppm from TMS) were used as internal standards. IR spectra were recorded for $CCl_4$ solutions on a UR-20 instrument, whereas UV spectra were recorded for heptane solutions on a Specord UV–vis instrument. Table 1 lists the data on the elemental composition of the compounds together with their IR and UV data. Table 2 lists the $^{19}F$ and $^{1}H$ NMR data.

### *Interaction of perfluoro-1-methylene-indan (3) with $HNO_3/HF$*

Freshly distilled anhydrous HF (8 ml), $HNO_3$ (0.6 g) and methylene-indan **3** (1 g) were poured in sequence into a nickel bomb (10 ml). The bomb was closed, the mixture stirred by shaking and stored for 10 h at 60–62 °C. It was then poured into ice/water, extracted with $CH_2Cl_2$, dried over $MgSO_4$ and the solvent distilled off. This gave 1.07 g of a mixture of 1-nitro-perfluoro-1-methyl-indan (**5**), 1-hydroxy-perfluoro-1-methyl-indan (**6**), perfluoro-1-(nitromethyl)indan (**7**) and perfluoro-indan-1-carboxylic acid (**8**) in the ratio 52:29:13:6 ($^{19}F$ NMR methods). On a silica gel column ($CH_2Cl_2$ as eluent), 0.66 g of a mixture of **5** and **7** (*c.* 4:1) and 0.21 g of alcohol **6** were isolated. All were further purified by short-path distillation (bath temperature, 60 °C; pressure, 5 mmHg).

Reactions of methylene-indan **3** with $HNO_3/SbF_5/HF$ ($HNO_3$ was added to an equimolar amount of $SbF_5$ in HF) and with $NO_2BF_4/HF$, as well as other experiments, were carried out in a similar way. The results are listed in Tables 3 and 4.

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*For Part 13, see ref. 1.

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TABLE 1. Elemental analyses, IR and UV data for compounds **5**–**7** and **11**

| Compound No. | Found/calculated (%) | | | Molecular formula | IR spectrum ($cm^{-1}$) | | | UV spectrum [$\lambda_{max}$, nm (l g $\epsilon$)] |
|---|---|---|---|---|---|---|---|---|
| | C | F | N(H) | | Fluorinated aromatic ring | $-NO_2$ asymm.[a] | Other bands | |
| **5** | 31.94<br>32.02 | 56.00<br>55.72 | 3.60<br>3.73 | $C_{10}F_{11}NO_2$ | 1527 | 1602 | 1417 | 272 (3.08) |
| **5**+**7** | 32.03<br>32.02 | 56.20<br>55.72 | 3.55<br>3.73 | $C_{10}F_{11}NO_2$ | 1523 | 1600 | 1415 | |
| **5**+**11** | 32.09<br>32.02 | 55.45<br>55.72 | 3.63<br>3.73 | $C_{10}F_{11}NO_2$ | 1524 | 1608;<br>1600 | 1416 | |
| **6** | 34.70<br>34.70 | 60.71<br>60.38 | (0.41)<br>(0.29) | $C_{10}HF_{11}O$ | 1524 | | 3585;<br>3300(OH);<br>1412 | 268 (2.98) |

[a] The symmetric stretching vibration band for the $NO_2$ group not been assigned because of the presence of other group absorptions in this region (1300–1360 $cm^{-1}$).

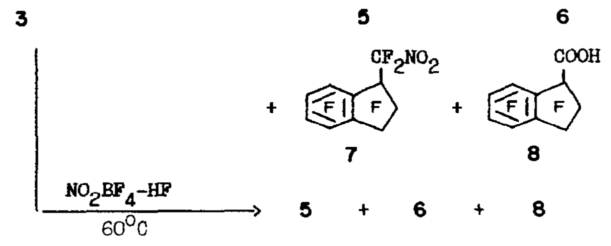
TABLE 2. $^{19}F$ NMR data for polyfluoroindanes[a]

| Compound No. | δ (ppm) | | | | | | | | | $J_{AB}$ (Hz) | $J_{A'B'}$ (Hz) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $F^1$ | $F^2$ | | $F^3$ | | $F^4$ | $F^{5,6}$ | $F^7$ | $CF_3$ ($CF_2NO_2$) | | |
| | | A | B | A' | B' | | | | | | |
| **5** | | 46.3 | 41.5 | 56.9 | 56.0 | 24.9 | 21.0; 21.4 | 33.0 | 95.7 | 249 | 262 |
| **6**[b] | | 39.4 | 33.0 | 57.9 | 53.2 | 23.5 | 16.6; 18.4 | 26.1 | 86.4 | 247 | 263 |
| **7** | −5.1 | 40.7 | 37.1 | 58.7 | 55.1 | 25.5 | 21.0; 21.7 | 29.5 | (69.4) | 252 | 262 |
| **11** | 19.0 | 19.0 | | 73.4 | 49.8 | 25.5 | 21.0; 21.6 | 30.4 | 90.6 | | 260 |

[a] For $CDCl_3$ solutions ($CCl_4$ for **6**).
[b] $^1H$ NMR spectrum in $CCl_4$: singlet at δ 3.71 ppm.

## Results and discussion

In the reaction of methylene-indan **3** with $HNO_3$ (purified from nitrogen oxides) in anhydrous HF (runs 9 and 10), the main products were 1-nitroperfluoro-1-methyl-indan (**5**) and 1-hydroxy-perfluoro-1-methyl-indan (**6**). The reaction mixture also contained perfluoro-1-(nitromethyl)indan (**7**) and perfluoro-indan-1-carboxylic acid (**8**). The total yield of compounds **5**–**8** was 90–93%. The introduction of 2 mol $H_2O$ per mol $HNO_3$ into the system (run 11) did not increase the content of the oxygen-containing derivatives **6** and **8**.



It should be noted that the system **3**/$HNO_3$/HF is heterogeneous, at least at *c.* 20 °C. However, the experimental results obtained were virtually independent of whether the process was conducted with stirring in a Teflon reactor or without stirring in a nickel bomb or Teflon reactor.

It has been shown via separate experiments that compounds **5**–**7** remain unchanged under the reaction conditions employed. Thus, mixtures of compounds **5** and **7** or **5**–**7** when heated with $HNO_3$/HF (runs 21 and 22) were recovered in 92–93% yield with the same ratio of components. In view of the possible replacement of the $NO_2$ group by F in the nitrofluorination products under the action of HF [6], and the formation of 1-hydroxyperfluoro-1-(nitromethyl)indan (**9**) from methyleneindan **3** and $HNO_3$ in the absence of HF [2], we have examined the possibility of the transformation of **9** to **6**. Under the same reaction conditions for compound **3** with $HNO_3$/HF, compounds **9** remained unchanged. The same applied to perfluoro-1-methyl-indan (**10**) which could formally lead to alcohol **6**. Moreover, we have shown that olefin **3** does not react (at 60 °C in HF) with NOF (run 20), whose formation in the

TABLE 3. Interaction of compounds **1–4** with nitrating agents in HF(7–8 g) at 60 °C (mol of nitrating reagent/mol of substrate = 3)

| Run No. | Substrate (g) | Nitrating agent (g) | Time (h) | Yield of mixture (g) | Mole ratio of products ($^{19}$F NMR data) | | | | | | Mol% substrate in mixture | Ratio **5/6** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | **5** | **6** | **7** | **8** | **10** | **11** | | |
| 1 | **1** (0.50) | $NO_2BF_4$ (0.77) | 10 | 0.53[a] | | | | | | | | |
| 2 | **2** (1) | $HNO_3$ (0.60) | 105 | 1.09 | 36 | 21 | | | | 43 | | 1.71 |
| 3 | **2** (1) | $HNO_3$ (0.60) | 60 | 1.09 | 37 | 20 | | | | 43 | 5 | 1.85 |
| 4 | **2** (1) | $HNO_3+SbF_5$ (0.66+2.28) | 69 | 1.02 | 29 | 20 | | | | 51 | | 1.45 |
| 5 | **2** (1.02) | $HNO_3+SbF_5$ (0.62+2.14) | 84 | 1.10 | 31 | 20 | | | | 49 | | 1.55 |
| 6 | **2** (0.50) | $NO_2BF_4$ (0.64) | 85 | 0.50 | 35 | 20 | | | 7 | 38 | | |
| 7 | **2** (0.79) | $NO_2BF_4$ (1.01) | 80 | 0.82 | 32 | 22 | | | 8 | 38 | | |
| 8 | **2** (0.69) | $NO_2BF_4$ (0.89) | 10 | 0.73 | 39 | 22 | | | | 39 | 40 | 1.77 |
| 9 | **3** (1) | $HNO_3$ (0.60) | 10 | 1.07 | 52 | 29 | 13 | 6 | | | | 1.79 |
| 10 | **3** (1) | $HNO_3$ (0.60) | 10 | 1.06 | 52 | 31 | 12 | 5 | | | | 1.68 |
| 11 | **3** (1) | $HNO_3+H_2O$[b] (0.60+0.35) | 20 | 1.04 | 52 | 29 | 15 | 4 | | | 4 | |
| 12 | **3** (0.98) | $HNO_3+SbF_5$ (0.60+2.05) | 10 | 0.98 | 45 | 28 | 5 | 22 | | | | 1.61 |
| 13 | **3** (1) | $HNO_3+SbF_5$ (0.70+2.46) | 10 | 1.06 | 43 | 29 | 5 | 23 | | | 10 | 1.48 |
| 14 | **3** (0.63) | $NO_2BF_4$ (0.81) | 10 | 0.65 | 44 | 30 | | 26 | | | | 1.47 |
| 15 | **3** (0.50) | $NO_2BF_4$ (0.64) | 10 | 0.51 | 45 | 30 | | 25 | | | | 1.50 |
| 16 | **3** (0.68) | $NO_2BF_4$ (0.87) | 80 | 0.72 | 35 | 31 | | 26 | 8 | | | |
| 17 | **4**[c] (1) | $HNO_3$ (0.53) | 50 | 0.87 | | | | | | | 100[c] | |

[a] 2-Nitroperfluoro-indan (**13**).
[b] Mole ratio $HNO_3/H_2O = 1:2$.
[c] Ratio of isomers *E*/*Z* = 2:1.

TABLE 4. Transformations of compounds **2**, **3**, **5–7** and **9–12** in HF (7–8 g) at 60 °C

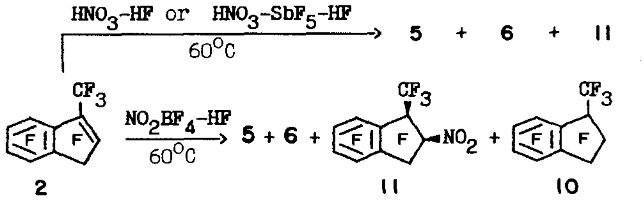
| Run No. | Substrates [mole ratio] (g) | Reagent (g) | Reaction time (h) | Yield of mixture (g) | Mole ratio of products ($^{19}$F NMR data) |
|---|---|---|---|---|---|
| 18 | **2**+**5**+**7** [62:30:8] (1.6) | $NO_2BF_4$ (1.32) | 80 | 1.65 | **2**/**5**/**6**/**7**/**10**/**11** = 9:44:13:6:3:25 |
| 19 | **2**+**12** [50:50] (0.98) | $NO_2BF_4$ (1.22) | 80 | 1.00 | **5**/**6**/**10**/**11**/**12**[a] = 19:18:3:22:38 |
| 20 | **3** (1) | NOF·3HF (1) | 113 | 0.96 | **3** |
| 21 | **5**+**6**+**7** [56:30:14] (1) | $HNO_3$ (0.6) | 10 | 0.92 | **5**/**6**/**7** = 56:30:14 |
| 22 | **5**+**7** [81:19] (1) | $HNO_3+H_2O$ (0.34+0.05) | 10 | 0.93 | **5**/**7** = 81:19 |
| 23 | **5**+**6**+**7** [52:35:13] (0.80) | | 10 | 0.75 | **5**/**6**/**7** = 51:36:13 |
| 24 | **5**+**6**+**7** [53:33:14] (0.80) | $SbF_5$ (0.80) | 4 | 0.70 | **5**/**6**/**7**/**10** = 8:43:12:37 |
| 25 | **5**+**7** [81:19:] (1) | $SbF_5$ (0.98) | 4 | 0.95 | **5**/**6**/**7**/**10** = 22:5:15:58 |
| 26 | **5**+**11** [40:60] (0.60) | $SbF_5$ (0.50) | 4 | 0.51 | **10**/**11** = 40:60 |
| 27 | **6** (0.74) | $SbF_5$ (0.78) | 4 | 0.68 | **6**/**10** = 16:84 |

[a] 2,2-Dihydroxyperfluoro-1-methyl-indan.

reaction of compound **3** with $HNO_3$/HF could not be excluded.

The reaction of methylene-indan **3** with $HNO_3$/HF in the presence of $SbF_5$ in an equimolar ratio with $HNO_3$ (runs 12 and 13) leads, as in the absence of $SbF_5$, to a mixture of compounds **5–8**. However, the nitro derivatives **5** and **7** were formed in smaller amounts, while the yield of acid **8** increased significantly. With $NO_2BF_4$/HF, methylene-indan **3** reacted (runs 14–16) to form a mixture of compounds **5**, **6** and **8**, with virtually no nitro derivative **7** being formed. It has been shown via a separate experiment (run 18) that compound **7** remained unchanged under these conditions.

The reactivity of the compounds with nitrating agents in HF decreased from methylene-indan **3** to compounds **2** and **4**. Thus, ethylidene-indan **4** did not react with $HNO_3$/HF at 60 °C (run 17), and it took much longer for indene **2** to be completely converted relative to methylene-indan **3**. The reaction products of indene **2** with $HNO_3$/HF (runs 2 and 3) were compounds **5**, **6** and *syn*-2-nitroperfluoro-1-methyl-indan (**11**). Compounds **5**, **6** and **11** were also formed as a result of the interaction of olefin **2** with $HNO_3$/HF in the presence of $SbF_5$ (runs 4 and 5). Relative to the reaction of indene **2** with $HNO_3$/HF, product **11** was formed in a higher, and product **5** in a lower, yield.



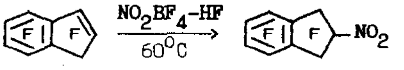
2 11 10

In the reaction of indene **2** with $NO_2BF_4$/HF (runs 6–8), a small amount of perfluoro-1-methyl-indan (**10**) was formed along with the products **5**, **6** and **11**. There was less nitro derivative **11** in the mixture as compared to the reactions of olefin **2** with $HNO_3$/HF and $HNO_3$/$SbF_5$/HF. The reaction mixture did not contain perfluoro-1-methyl-2-indanone (**12**), which corresponds to addition of the oxygen function to position 2 of compound **2**. At the same time, it has been shown via a separate experiment (run 19) that ketone **12** obtained in a different way [1] and added to indene **2** may be recovered in *c*. 85% yield from the reaction with $NO_2BF_4$/HF.

Indan **10** seems to be mainly formed by replacement of the $NO_2$ group by F in indan **5** under the reaction conditions employed. Indeed, with a decreased degree of conversion of indene **2** (run 8), a mixture of products **5**, **6** and **11** was formed, with compound **5** being present in a greater amount and indan **10** virtually absent. In contrast, when the reaction time for methylene-indan **3** with $NO_2BF_4$ was increased from 10 h to 80 h, the reaction (run 16) led to a mixture containing a small amount of indan **10** along with products **5**, **6** and **8**, with the content of nitro derivative **5** being diminished. The relative content of the remaining compounds in the mixture with respect to the changed olefins **2** or **3** was virtually independent of the reaction time.

Exchange of the $NO_2$ group by F in the nitro-indan **5** is evidently promoted by the Lewis acid $BF_3$ formed in the reaction. This agrees with the observation that the mixture of compounds **5**–**7** remained unchanged on heating with anhydrous HF (run 23), while heating in HF/$SbF_5$ (run 24) led to methyl-indan **10**. It has been shown by separate experiments (runs 24–26) that nitro-indan **5** is transformed in HF/$SbF_5$ not only to the product **10** but also to alcohol **6**, which under these conditions (run 27) also gave methyl-indan **10**. Hence, it is not improbable that in the reaction of compound **2** with $NO_2BF_4$/HF, methyl-indan **10** may be formed not only from the nitro derivative **5** but also in part from alcohol **6**.

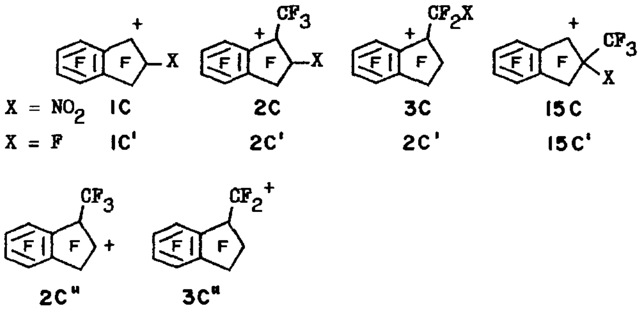
Thus, substrates **2** and **3** react with nitrating agents in HF to give, along with nitrofluorination products, compounds **6** and **8** corresponding to the addition of the oxygen function to the substrate molecule; in the reaction of methylene-indan **3** with $NO_2BF_4$, their share is more than one-half of the total. In this connection, we have studied the reaction of indene **1** with $NO_2BF_4$/HF. We have shown (run 1) that, as in the reaction with $HNO_3$/HF [5], 2-nitro-perfluoro-indan (**13**) is formed with no other products being found in the mixture.



1 13

The reaction seems to proceed via an electrophilic mechanism, as in the transformation of compound **1** in the presence of $HNO_3$/HF. The orientation in this process agrees both with the charge distribution at a multiple bond in the substrate [7] and with the relative stability of the intermediate cation [5]. It is most likely that the same factors determine the formation of 2-nitro-perfluoro-2-methyl-indan (**14**) in the reaction of perfluoro-2-methyl-indene (**15**) with $HNO_3$/HF [8].

A more complex situation arises in the reactions of compounds **2** and **3** with nitrating agents in HF. Thus, in order to analyse the experimental results, we have carried out quantum-chemical calculations using a standard MNDO approximation [9] for compounds **1**–**3** and **15**, their radical cations **1RC**–**3RC** and **15RC**, the nitro-perfluoro-indanyl cations **1C**–**3C** and **15C**, the perfluorinated indanyl cations **1C′**, **2C′**, **2C″**, **15C′**, and for the perfluoro(1-indanyl)methyl cation **3C″**. For open-shell systems, we used the restricted Hartree–Fock method.



For compounds **2** and **3**, the calculations were performed with full geometry optimization. The carbon frame and the F atoms at the $sp^2$ carbon atoms were found to lie in virtually the same plane. Thus, in compound **3** the exocyclic $CF_2$ group deviates out of plane more than the other groups, but the angle between the multiple bond and molecular plane is as little as 1°. In indene **2** only the F atom in the 2-position deviates from the plane, the angle between the C−F bond and molecular plane being *c*. 0.2°. In this connection, in the case of indenes **1** and **15**, geometry optimization was carried out only for those structures where all the fragments other than the C($sp^3$)−F bonds lie in the same plane. For the radical cations **1RC**–**3RC** and **15RC**, the geometry assumed was that of their neutral precursors (cf. ref. 10). Geometry optimization of all closed-shell cations was carried out on the assumption that the aromatic ring and its C−F bonds lie in the same plane. Tables 5 and 6 give some results of such calculations.

As seen from Tables 5 and 6, the charge distribution at a multiple bond in substrates **2** and **3**, and the relative stability of the intermediate cations (cf. enthalpies of formation of ions **2C′**, **2C″** and **3C″**) must influence the orientation of the electrophilic addition of the reagent at the bond in opposite directions. The nitro derivatives **7** and **11** may be assumed to be the products formed in agreement with the relative stability of the intermediate cations, and nitro-indan **5** to be the product of $NO_2^+$ addition at the multiple bond of compounds **2** and **3** in conformity with the charge distribution at the bond. Since alcohol **6** and acid **8** are not the transformation products of the nitro derivatives **5** and **7** under the reaction conditions employed, their formation may be formally explained as being the result of the interaction of compounds **2** and **3** with the oxygen atom of $NO_2^+$. However, this seems to be unlikely. Indeed, as far as we know, $NO_2^+$ is not an O-electrophile. Moreover, the authentic O-electrophile $HO^+$ does not give alcohol **6** on reaction with olefins **2** and **3**, but leads to ketone **12** and acid **8**, respectively [1]; in the reaction of compound **2** with nitration reagents in HF, ketone **12** is totally absent from the reaction products.

We have also considered other possible routes for the process. However, it does seem that the results on the whole may be most adequately explained as in Scheme 1. Thus, for example, with methylene-indan **3**, $NO_2^+$ probably initially adds at the multiple bond of substrate **3** in accordance with the relative stability of the cation **3C**; addition of $F^-$ to the latter gives the nitro derivative **7**. The formation of acid **8** may be depicted as being the result of the isomerization of the ion **3C** to the cation **3C‴** followed by further transformations of the latter. Isomerization of the ion **3C** possibly proceeds via an intermediate radical pair [**3RC**, $NO_2$•], where recombination of the radicals ONO• and **3RC** takes place inside the reaction cell in accordance with the relative stability of the cation **3C‴** formed. This assumption agrees with previous results [11] and with data on the isomerization of 1-nitropolymethylbenzeneonium ions to cations with an oxygen-containing function [12] formed from the oxygen atoms of the nitro group [12, 13].

Interaction of the radical cation **3RC** with $F^-$ (cf. ref. 14) should lead to the formation of the perfluoro-1-methyl-1-indanyl radical (**16**) in accordance both with the relative stability of the latter and with the charge distribution in **3RC**. Addition of $NO_2$• to radical **16** at the nitrogen or oxygen atom will give compounds **5** and **6**, respectively. It should be noted that in the radical addition of $N_2O_4$ the olefins **2** and **3**, an N-product similar to **5** also prevails relative to the O-product [2].

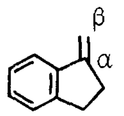
The reaction of methyl-indene **2** with nitrating reagents in HF may be represented by a similar scheme as for isomer **3**. According to this scheme, compounds **5** and **6** are formed from olefins **2** and **3** by recombination of the same radicals **16** and $NO_2$•. Because of this, one would expect a similar ratio of products **5** and **6** in the reaction of olefins **2** and **3** with the same nitration reagent (for $HNO_3$/HF and $HNO_3$/$SbF_5$/HF) and the ratio (**5**+**10**)/**6** for $NO_2BF_4$/HF if compound **10** is obtained mainly from the nitro derivative **5**. Indeed, in the case of $HNO_3$/HF and $HNO_3$/$SbF_5$/HF, we have observed the expected result. However, for the system $NO_2BF_4$/HF no such correspondence was observed. This may be due to the fact that indan **10** is formed not only from nitro derivative **5** but also from alcohol **6**. However, account should be taken of the fact that the above product ratio only holds for compounds **2** and **3** provided that formation of the radical pair **16** and $NO_2$• occurs in the process. If this pair, together with [**2RC**, $NO_2$•] and **2C** or [**3RC**, $NO_2$•) and **3C**, only simulates a transition state (and this is different for **2** and **3**), then the ratio may change.

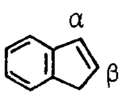
The fact that nitro derivative **7** is absent from the reaction mixtures or its content is significantly smaller than the content of compound **11** suggests that cation **3C** is more readily transformed into the radical pair [**3RC**, $NO_2$•] than the ion **2C** is transformed into the pair [**2RC**, $NO_2$•]. Because of this, the radical cation **2RC** is scavenged by the fluoride anion, possibly at an earlier stage in the formation of this pair from the ion **2C** relative to scavenging of radical ion **3RC** in the

TABLE 5. Calculated enthalpies of formation of compounds and cations (kcal $mol^{-1}$)

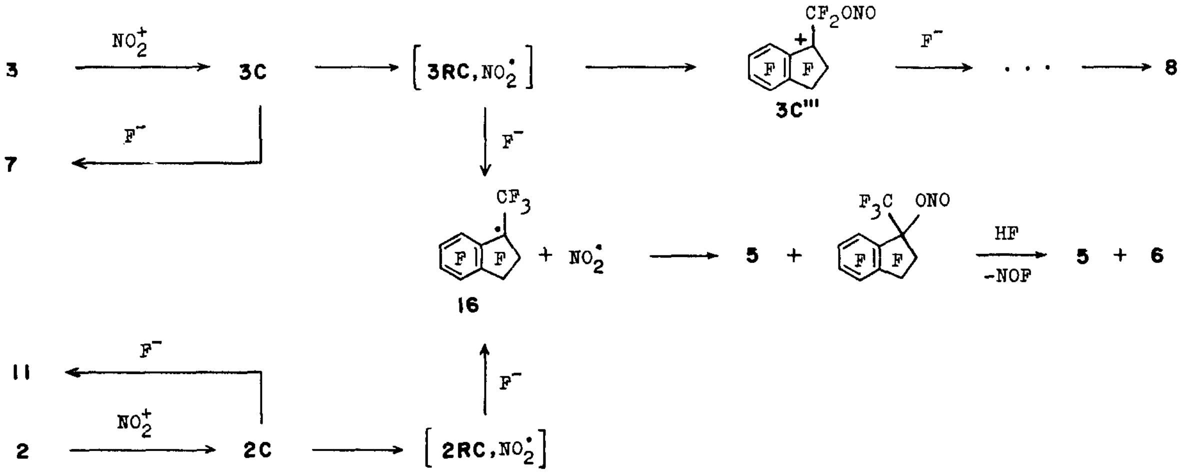
| Compound | $-\Delta H_f$ | Compound | $-\Delta H_f$ | Compound | $-\Delta H_f$ | Compound | $-\Delta H_f$ |
|---|---|---|---|---|---|---|---|
| **1** | 313.54 | **2** | 411.74 | **3** | 409.80 | **15** | 413.58 |
| **1RC** | 78.10 | **2RC** | 170.44 | **3RC** | 173.45 | **15RC** | 164.89 |
| **1C** | 66.21 | **2C** | 145.72 | **3C** | 146.33 | **15C** | 153.68 |
| **1C′** | 139.87 | **2C′** | 219.87 | | | **15C′** | 227.33 |
| | | **2C″** | 204.34 | **3C″** | 213.57 | | |

TABLE 6. Quantum-chemical data for compounds 1–3 and 15, and their radical cations





| Compound No. | $E_{HOMO}$ (eV) | Charge | | HOMO coefficients | | | | Charge | | Unpaired electron density | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $q_\alpha$ | $q_\beta$ | $c_\alpha$ | $c_\beta$ | Compound No. | $E_{HOMO}$ (eV) | $q_\alpha$ | $q_\beta$ | $\rho_\alpha$ | $\rho_\beta$ |
| **1** | −10.48 | 0.17 | 0.04 | 0.38 | 0.49 | **1RC** | −15.59 | 0.23 | 0.23 | 0.13 | 0.23 |
| **2** | −10.75 | −0.16 | 0.18 | 0.29 | 0.33 | **2RC** | −15.84 | −0.16 | 0.33 | 0.11 | 0.13 |
| **3** | −10.57 | −0.24 | 0.48 | 0.35 | 0.33 | **3RC** | −15.56 | −0.22 | 0.63 | 0.14 | 0.11 |
| **15** | −11.05 | 0.33 | −0.31 | 0.18 | 0.40 | **15RC** | −16.17 | 0.30 | −0.12 | 0.05 | 0.20 |



Scheme 1.

pair [**3RC**, $NO_2\bullet$]. Under these circumstances, product **12** corresponding to recombination of **2RC** and ONO• is not formed.

The assumption of an easier transformation for cation **3C** relative to ion **2C** to the corresponding radical cations and $NO_2\bullet$ agrees with the calculated enthalpy of the gas-phase process. Thus, for ions **15C**, **1C**, **2C** and **3C**, this enthalpy is equal to −3.31, −3.99, −16.82 and −19.22 kcal $mol^{-1}$, respectively. Such values were calculated using the enthalpies of formation of the cations and radical cations obtained by quantum-chemical calculation (Table 5) and the experimental value of 7.9 kcal $mol^{-1}$ for $NO_2\bullet$ from ref. 9. If the reaction enthalpy is taken as a reference point in the case of the formation of radical cation **15RC** from cation **15C** (or from **15C'**), then the relative enthalpies of this reaction for the radical cations **15RC**, **1RC**, **2RC** and **3RC** will amount to 0(0), −0.68 (−0.67), −13.51 (−13.01) and −15.91 (−16.02) kcal $mol^{-1}$, respectively. It should be noted that the process is only thermodynamically favourable for the formation of radical cations from cations **C** containing the nitro group and is unfavourable for their formation from the corresponding perfluorinated indanyl cations **C'**. The relative energies of the process, however, are virtually unchanged and may be modelled using perfluorinated analogues.

Thus, in the reaction of the series of compounds **15**, **1**, **2** and **3** with nitrating agents in HF, the content of those products corresponding to intermediate formation of the substrate radical cations increases, although for compounds **1** and **15** no such products seem to be formed. Thermodynamic data on the conversion of the ions formed by $NO_2^+$ addition at the multiple bond of a substrate to these radical cations increase in the same series. It should be noted that the ionization potential of the olefins decreases in the series **15**, **2**, **3** and **1**.

The structures of compounds **5–7** and **11** have been confirmed by elemental analyses and spectral data. The *cis* position of the $NO_2$ and $CF_3$ groups relative to the plane of the five-membered ring in compound **11** has been assigned by analogy with ref. 2, based on an analysis of the fine structure of the $CF_3$ signal (d, 21 Hz; d, 6 Hz; d, 3 Hz) in the $^{19}F$ NMR spectrum.

Methyl-indan **10** was identified in mixtures via the $^{19}F$ NMR spectrum which coincided with that of an authentic sample [15].

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