

# THE NITRATION OF FLUOROTOLUENES AND FLUOROXYLENES. PRODUCT ANALYSIS BY GAS-LIQUID CHROMATOGRAPHY

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## INTRODUCTION

In the nitration of fluorotoluenes<sup>1</sup> and fluoroxylenes<sup>2</sup> the introduction of the nitro group permits a separation of the isomers by fractional distillation. A stable b.p. after repeated fractionations was taken as proof of purity, and such fractions were identified by conversion to derivatives of known characteristics.

The strong directing power of fluorine and the fact that the fluorinated and the corresponding fluorine-free aromatic hydrocarbons have nearly identical b.p.<sup>4</sup>, permitted the assumption that: (a) if one compound is produced in greater amount the nitro group will be positioned *para* to fluorine, and (b) the b.p. sequence in fluoronitrotoluenes and -xylenes will be the same as the b.p. sequence of the fluorine-free nitrotoluenes and -xylenes<sup>2</sup>. It would seem, therefore, that gas-liquid chromatography offers an accurate and rapid method for the study of these reaction products.

An efficient silicone oil, DC-200, column was found best for the separation of the nitration products of fluorotoluenes and -xylenes. Apiezon L columns have been recently used for the separation of mono-<sup>5</sup> and dinitrotoluene<sup>6</sup> isomers, while for the separation of the chloronitrobenzene isomers polar columns are recommended<sup>7</sup>. The behaviour of fluoronitrotoluenes and -xylenes is more like that of the nitrotoluenes than the chloronitrobenzenes since the fluorinated isomers have differences in b.p. similar to the fluorine-free isomers. Separation efficiencies in the non-polar columns are measured by b.p. differences<sup>8</sup>.

## EXPERIMENTAL AND RESULTS

The nitration of the fluorotoluenes was performed with fuming nitric acid at  $-10^{\circ}$  as described by SCHIEMANN<sup>1</sup>. The nitration of the fluoroxylenes, except for greater cooling, was achieved under similar conditions<sup>2</sup>. The fluorotoluenes and -xylenes were prepared, by means of the Schiemann fluoroborate process<sup>9</sup>, from the corresponding amines of 99% claimed purity (puriss., "Fluka", Switzerland), which was confirmed by preparing derivatives reported in the literature<sup>10</sup>.

The crude product of the nitration reaction was fractionated and the mononitrated products were collected (fractions boiling  $95-130^{\circ}/14$  mm). These in all cases gave a satisfactory analysis (C, H, F, N) and gas chromatographic results identical to the ones obtained for the crude reaction product. Dinitration did not occur in detectable amounts under the conditions employed.

The gas chromatographic analysis gave a very good separation and the elution sequence was identical to the b.p. order. Compounds like 2-fluoro-3-nitrotoluene and 2-fluoro-5-nitrotoluene which give the same fluorine-free nitrotoluene could not be separated, so that such pairs appeared in one chromatographic peak. In evaluating the chromatograms obtained, percentages of peak areas were taken for percentages of composition. Analyses of known mixtures have shown that a molar response correction coefficient is not required.

All fluoroxylenes except fluoro-*p*-xylene gave chromatographic peaks for a number of fluoronitroxylenes equal to the places free for substitution. Fluoro-*p*-xylene gave up to 94 % 2-fluoro-5-nitro-1,4-xylene together with two by-products as a shoulder of the main peak. *o*-Fluorotoluene gave three and the *meta*-isomer two peaks for mononitration products. *p*-Fluorotoluene and 4-fluoro-1,2-xylene could not be nitrated under the conditions described and gave nitroxylenols and nitrocresols instead<sup>1,2</sup>.

Infrared spectral analysis was used to identify the different isomers, the spectra of which in the low frequency region, 900–750 cm<sup>-1</sup>, are characteristic. For the main components samples could be obtained gas chromatographically pure by distillation and then recrystallisation from methanol<sup>2</sup>. Minor reaction products were collected after gas chromatographic separation.

#### DISCUSSION

Of the four expected chromatographic peaks for the 2-fluoronitrotoluenes only three were obtained (Fig. 1-A), the pair 2-fluoro-3-nitrotoluene and 2-fluoro-5-nitrotoluene appearing together. The amounts of isomer were calculated by means of the partial rate factors of nitration of fluorobenzene<sup>11</sup>, which should be a good approximation. The products I, II and III (see Table I) were isolated by fractional distillation and characterised as described previously<sup>3</sup>, but the composition of 6 % of I, 84 % of II and 10 % of III given in the literature and the fact that the fourth isomer (IV) was not mentioned disagrees with our results.

The nitration of *m*-fluorotoluene should give three isomeric products, all of which were identified and characterised<sup>1</sup>. The main product (V) and the third isomer (VII) have nearly the same b.p. and appear together in the chromatogram (Fig. 1-B). This was confirmed by I.R. analysis of the product of the chromatographic peak where additional absorption bands due to 1-, 2-, 3- substitution were easily recognised. To calculate the percentage of substitution in VII it was assumed that steric effects are not important in the approach of the nitronium ion to the two positions *ortho* to fluorine, as toluene nitrated under similar conditions<sup>12</sup> gave 41 % *ortho*- and 59 % *para*-nitrotoluene. Therefore in this case it would be expected that the yield of VII would be 70 % of (VI) or 16 % of the nitration products (literature data<sup>1</sup> give a composition of 7.5 % for (VI), 83 % for (V) and 4.5 % for (VII)).

The study of the nitration of fluoroxylenes is simpler in that a smaller number of isomers is expected and the differences in b.p. are greater. Thus, gas chromatography permits a good separation of all isomers (Figs. 1-C, 1-D and 1-E), the identification of which has been described<sup>2</sup> and later confirmed by I.R. analysis.

3-Fluoro-6-nitro-1,2-xylene (VIII) is the main product of the nitration of 3-fluoro-1,2-xylene appearing first in the chromatogram (Fig. 1-C). The isomer with the

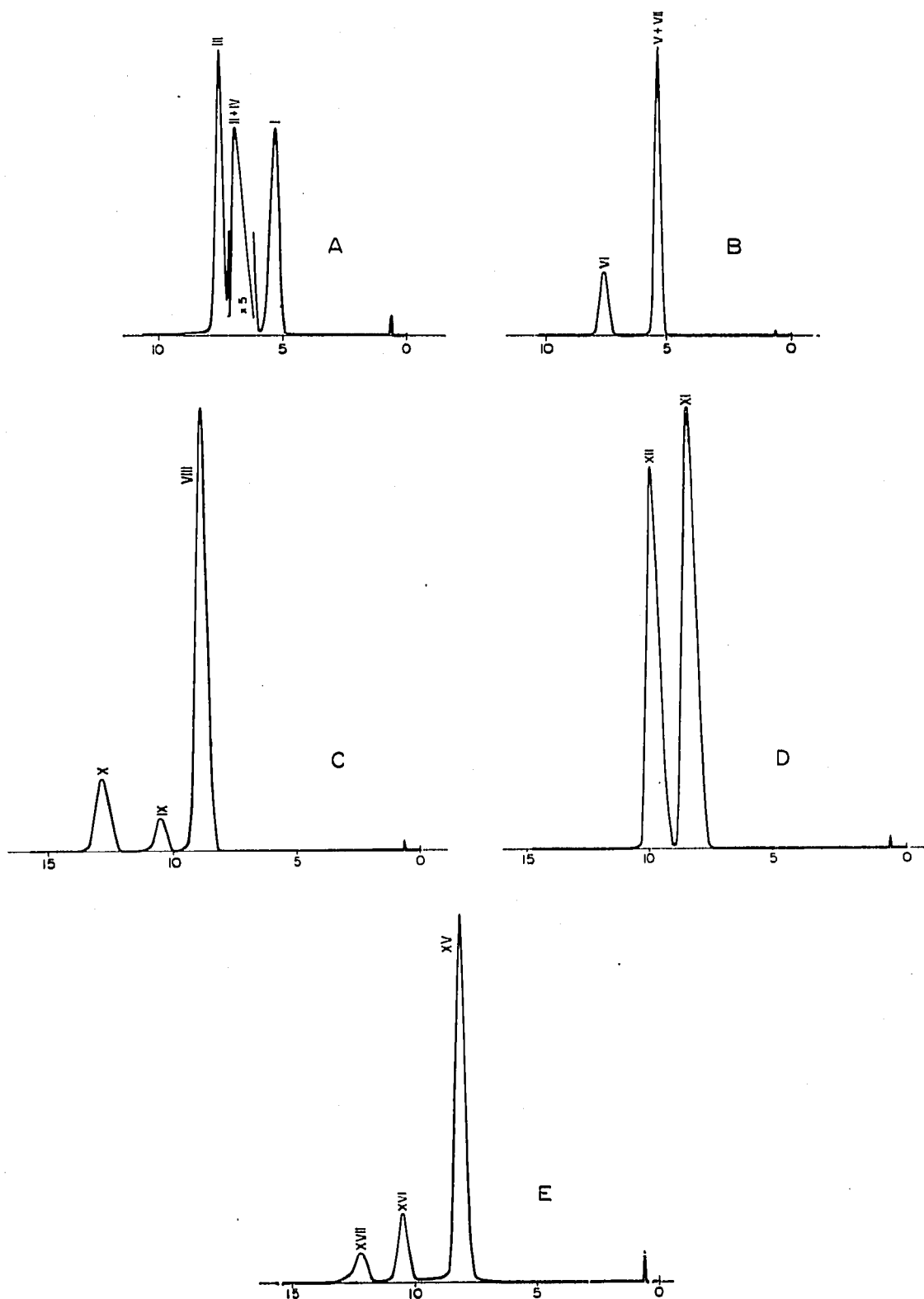


Fig. 1. Analysis of the nitration products of A: *o*-fluorotoluene; B: *m*-fluorotoluene; C: 3-fluoro-1,2-xylene; D: 2-fluoro-1,3-xylene; E: 4-fluoro-1,3-xylene. Conditions for chromatography: Chromatograph: Perkin-Elmer Fraktometer Model 116; column dimensions: 200 × 0.635 cm O.D.; solid support: Chromosorb R (60/80); stationary phase: Silicone Oil DC-200 (20:80); temperature: 191°; carrier gas: helium at 86 ml/min; detector: thermistor at 8 mV; recorder: 2.5 mV; 1 sec; 0.5 cm/min.

TABLE I

ISOMER DISTRIBUTION IN THE NITRATION OF FLUOROTOLUENES AND FLUOROXYLENES AND PHYSICAL PROPERTIES OF FLUORONITROTOLUENES AND FLUORONITROXYLENES

	Compound	%	b.p. <sup>b</sup> (°C/mm)	m.p. <sup>b</sup> (C°)
<i>o</i> -Fluorotoluene				
I	2-Fluoro-6-nitro-toluene	10.2	97-97.2°/11	—2
II	2-Fluoro-5-nitro-toluene	68.0	99.4-99.6°/13	41.5
III	2-Fluoro-4-nitro-toluene	12.2		
IV	2-Fluoro-3-nitro-toluene	9.6 <sup>a</sup>		
<i>m</i> -Fluorotoluene				
V	3-Fluoro-6-nitro-toluene	61.2	97-98°/10	27-28
VI	3-Fluoro-4-nitro-toluene	22.8	—	53.2
VII	3-Fluoro-2-nitro-toluene	16.0 <sup>a</sup>	92.4-92.8°/12	17.5-18
<i>3</i> -Fluoro- <i>1,2</i> -xylene				
VIII	3-Fluoro-6-nitro- <i>1,2</i> -xylene	75.8	109-110°/14	36-37
IX	3-Fluoro-5-nitro- <i>1,2</i> -xylene	6.1		
X	3-Fluoro-4-nitro- <i>1,2</i> -xylene	18.1	126-127°/14	
<i>2</i> -Fluoro- <i>1,3</i> -xylene				
XI	2-Fluoro-4-nitro- <i>1,3</i> -xylene	52.6	107-108°/14	
XII	2-Fluoro-5-nitro- <i>1,3</i> -xylene	47.4	111-112°/14	42-43
<i>5</i> -Fluoro- <i>1,3</i> -xylene				
XIII	5-Fluoro-2-nitro- <i>1,3</i> -xylene	61.2	93-94°/14	51-52
XIV	5-Fluoro-4-nitro- <i>1,3</i> -xylene	38.8	102-103°/14	50-51
<i>4</i> -Fluoro- <i>1,3</i> -xylene				
XV	4-Fluoro-6-nitro- <i>1,3</i> -xylene	75.5	108-109°/14	
XVI	4-Fluoro-2-nitro- <i>1,3</i> -xylene	16.3		
XVII	4-Fluoro-5-nitro- <i>1,3</i> -xylene	8.2		
<i>2</i> -Fluoro- <i>1,4</i> -xylene				
XVIII	2-Fluoro-5-nitro- <i>1,4</i> -xylene	93.7	107-107.5°/14	50-51

<sup>a</sup> Calculated.<sup>b</sup> The physical constants for fluoronitrotoluenes and fluoronitroxylens are taken from refs. 1 and 2, respectively.

higher retention time gave an infrared spectrum indicating two adjacent hydrogen atoms, which is the case with (X).

The two symmetrical fluoro-*1,3*-xylenes, 2-fluoro-*1,3*-xylene and 5-fluoro-*1,3*-xylene each gave rise to two isomeric nitration products, which were well separated and easily characterised. In the case of nitration of 2-fluoro-*1,3*-xylene the substitution *para* to fluorine is a little less than double the partial rate of substitution *meta* to fluorine, though in the case of 5-fluoro-*1,3*-xylene substitution in the position *para* to fluorine is larger, this owing to the unusually low reactivity of positions *ortho* to fluorine<sup>13</sup>.

The nitration of 4-fluoro-1,3-xylene gave on gas chromatographic analysis (Fig. 1-E) three fluoro-nitroxylens to which structures could be assigned. The main product of substitution is also the isomer with the lower b.p.; it gave an infrared spectrum for two adjacent hydrogen atoms consistent with the 4-fluoro-6-nitro-1,3-xylene structure (XV). Of the two other isomers 4-fluoro-2-nitro-1,3-xylene (XVI) appears second in the chromatogram while the minor component 4-fluoro-5-nitro-1,3-xylene (XVII) appears third. In interpreting these results we should take into account that the nitration of 4-fluoro-1,3-xylene also gives a 6–8 % yield of nitroxyleneols<sup>2</sup>.

2-Fluoro-1,4-xylene gave 93.7 % nitration *para* to fluorine. Upon pouring the crude nitration reaction product on ice 2-fluoro-5-nitro-1,4-xylene (XVIII) crystallises in fine needles. The other two minor products expected appeared as a shoulder in the chromatogram and they could not be further separated for identification purposes.

Out-of-plane bending –CH absorption is reported to move towards higher frequencies in the nitrated aromatic compounds<sup>14</sup>. However, in all cases it has been demonstrated that absorption in the low frequency region below 900  $\text{cm}^{-1}$  is not seriously affected by the order of substitution<sup>14</sup>. This was found to hold here in that fluoronitroxylens of different order in substitution, such as 2-fluoro-5-nitro-1,4-xylene, 2-fluoro-5-nitro-1,3-xylene, and 3-fluoro-6-nitro-1,4-xylene, gave rise to well located characteristic absorptions due to isolated hydrogen atoms at 890–900  $\text{cm}^{-1}$ . The spectra of 2-fluoro-5-nitro-1,4-xylene and 4-fluoro-6-nitro-1,3-xylene are representative of the infrared spectra obtained (Figs. 2 and 3).

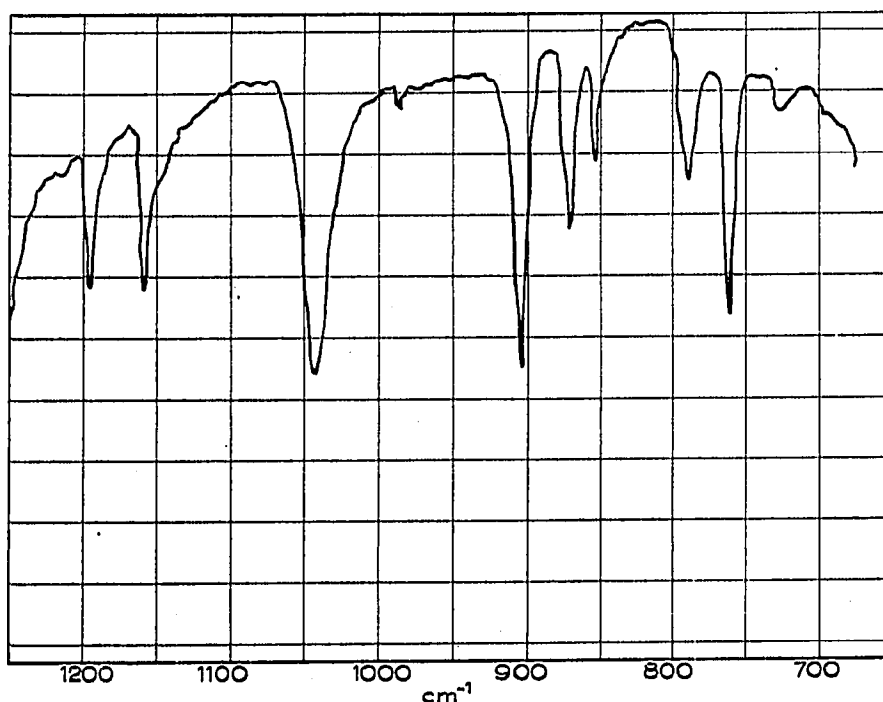


Fig. 2. Infrared spectrum in the low frequency region (1250–650  $\text{cm}^{-1}$ ) of 2-fluoro-5-nitro-1,4-xylene.

The same consistency was also found in the 1-, 2-, 3-, 4-substitution cases. A strong band due to two adjacent hydrogen atoms for three isomeric 1-, 2-, 3-, 4-substituted fluoronitroxylens appears between 823 and 827  $\text{cm}^{-1}$ , namely, 3-fluoro-6-

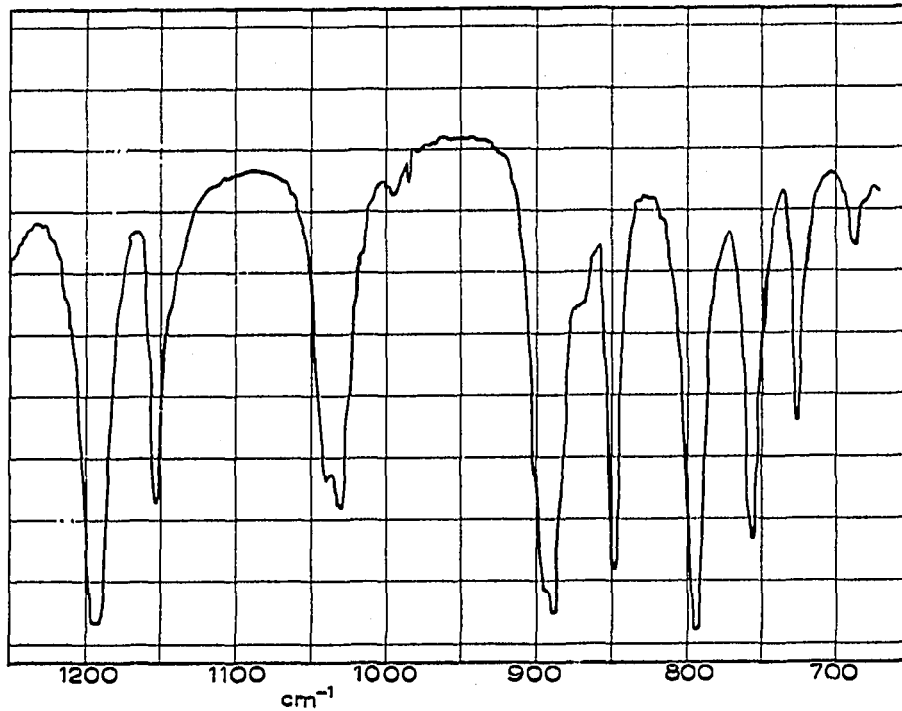


Fig. 3. Infrared spectrum in the low frequency region ( $1250-650\text{ cm}^{-1}$ ) of 4-fluoro-6-nitro-1,3-xylene.

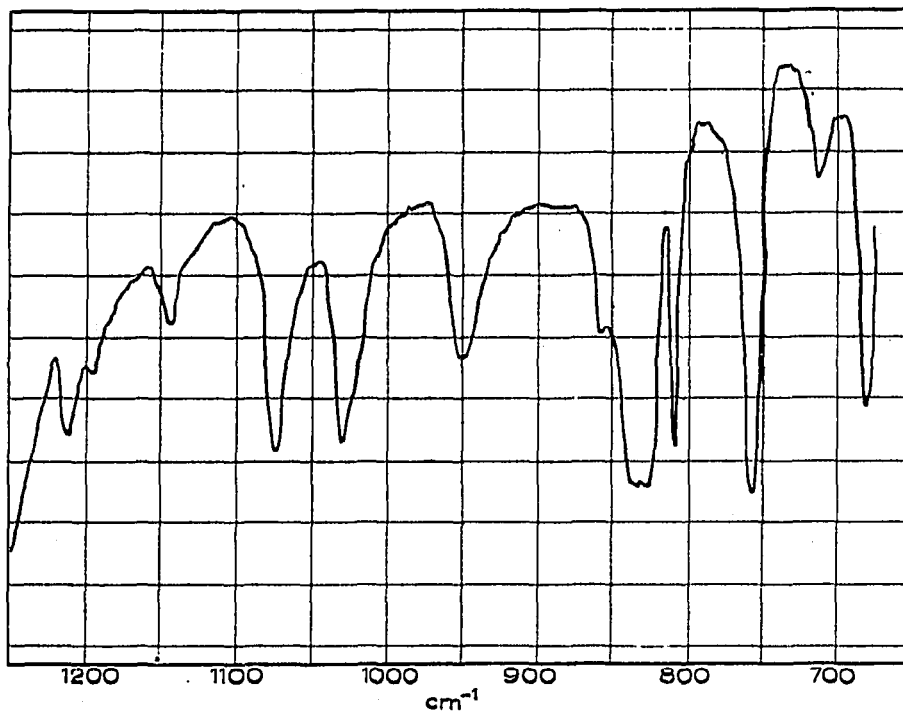


Fig. 4. Infrared spectrum in the low frequency region ( $1250-650\text{ cm}^{-1}$ ) of 3-fluoro-6-nitro-1,2-xylene.

nitro-1,2-xylene ( $823\text{ cm}^{-1}$ ), 3-fluoro-4-nitro-1,2-xylene ( $826\text{ cm}^{-1}$ ) and 2-fluoro-4-nitro-1,3-xylene ( $827\text{ cm}^{-1}$ ). Fig. 4 gives the infrared spectrum of 3-fluoro-6-nitro-1,2-xylene as representative of the class.

## SUMMARY

The distribution of products in the nitration of fluorotoluenes and fluoroxylenes is determined by gas-liquid chromatography on a silicone oil DC-200 column. The nitration of the four isomeric fluoroxylenes and two isomeric fluorotoluenes studied was found to give high percentages of products with the nitro-group *para* to fluorine but they were not as high as previously reported by other methods of analysis.

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