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Abstract

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NITRATION OF TRIPHENYLOXONIUM AND DIPHENYLHALOGENONIUM CATIONS

We have studied the nitration of salts previously obtained and described by us (1)—namely, the borofluorides—of diphenylchloronium, diphenylbromonium, and triphenyloxonium. In the nitration of both diphenylhalogenoniums with a strong nitrating mixture, the nitro group, both at room temperature and at 100°, enters almost exclusively into the meta position, forming, in good yield, the di-*m*-nitrodiphenylhalogenonium salt. The meta orientation in these reactions is expressed still more sharply than in the case of diphenyliodonium borofluoride (72% meta and 28% para). The reaction rate decreases in the series:

$$(C_6H_5)_2I^+ > (C_6H_5)_2Br^+ > (C_6H_5)_2Cl^+.$$

In principle, therefore, the orientation of nitration of diphenylhalogenonium salts obeys the general regularity of nitration of aromatic onium salts—meta orientation. Indeed, nitration of the salts of phenyltrimethylammonium (2), phenyltrimethylphosphonium (3), phenyldimethylsulfonium, and phenyldimethylselenonium (4) takes place entirely in the meta position. Nitration of the phenyltrimethylarsonium salt (3) gives 98% of the meta isomer; of the phenyltrimethylstibonium salt (3), 86%; and of the diphenyliodonium salt (5), 80% of the meta isomer.

Nitration of triphenyloxonium borofluoride does not proceed even with a strong nitrating mixture (1 part HNO_3, $d = 1.52$, and 1.5 parts H_2SO_4, $d = 1.84$) at room temperature. This substance, which is extraordinarily inert toward electrophilic substitution reactions, could be nitrated by this mixture only on heating to 100° for 60 hours. In this way almost pure tri-*p*-nitrotriphenyloxonium borofluoride is obtained in 80% of theory. Thus, the triphenyloxonium cation is an astonishing exception among all known phenyl onium cations. Suspecting the possibility of a radical course of para-nitration (at the expense of HNO_2 and nitrogen oxides) under such severe conditions, we carried out, under exactly the same conditions, the nitration of the borofluorides of triphenylsulfonium, phenyltrimethylammonium, and diphenylbromonium. These onium salts, under the given conditions as well, were nitrated almost entirely in the meta position. On the other hand, nitration of triphenyloxonium borofluoride with NO_2BF_4, which proceeds already at room temperature, gives, in 92% yield, the borofluoride of the same tri-*p*-nitrotriphenyloxonium.

schematic comparison of phenyl onium cations and halobenzenes

Figure 1: schematic comparison of phenyl onium cations and halobenzenes

Thus, para orientation of electrophilic substitution in the triphenyloxonium cation is an exceptional experimental fact in the series of onium compounds. It is unlikely that the special behavior of the triphenyloxonium cation is explained by steric causes. Comparison with the triphenylcarbonium cation, which is nitrated entirely in the meta position (^{6}), can convince one of this. $(C_6H_5)_3C^+$ has a propeller-like distorted planar form. The distinction of triphenyloxonium from triphenylcarbonium must be a more trigonal-pyramidal form (the presence of a lone pair of electrons). In this case, the consequence should be a rotation of the planes of the phenyls about the C—O axis relative to the faces of the trigonal pyramid, more pronounced than the propeller-like rotation of the phenyls in $(C_6H_5)_3C^+$. Such a rotation should, on the one hand, diminish steric hindrances (and in $(C_6H_5)_3C^+$ these hindrances do not affect attack at the meta position), and, on the other hand, to one degree or another

should withdraw the lone pair of electrons from conjugation (completely upon rotation by 90°). Both factors would favor meta orientation.

Apparently, the only conceivable reason for the unusual behavior of triphenyloxonium upon nitration may be the same reason that causes ortho-para orientation in electrophilic substitution in halobenzenes, including fluorobenzene. It is of interest to compare the orientation of electrophilic substitution in a series of phenyl onium cations with one another, with the triphenylcarbonium cation, and also with halobenzenes.

It is obvious that the triphenyloxonium cation has in common with all the listed substances the property of a negative inductive effect of the key atom. In contrast to carbonium and ammonium, and similarly to sulfonium and halogenonium, the key (oxygen) atom of oxonium has a lone pair of electrons. Like the nitrogen of ammonium, and unlike sulfur and haloids, expansion of the octet of oxonium oxygen is impossible. All this creates the prerequisites for the following explanation: the very strong negative inductive effect of oxonium oxygen, which strongly passivates the phenyl nuclei, is nevertheless offset, as in halobenzenes, by conjugation of the lone pair of electrons of the oxygen atom with the π-electrons of the phenyls ($+T$-effect). In halogenoniums, the electron pairs are already so passive that they manifest themselves only in diphenyliodonium (20% yield of the para-nitro compound). In triphenylsulfonium, the intrinsically conceivable conjugation of the sulfur electron pair (+ tautomeric effect) is outweighed by the (—) tautomeric effect, owing to the possibility of drawing the π-pair of the phenyl into the vacant sulfur shell as a consequence of the possibility of octet expansion. This possibility is also present in the halide of halogenoniums, but is absent in the nitrogen of ammoniums. However, the nitrogen of ammoniums also has no lone pair that could give rise to a $+T$-effect. The result is pure meta orientation due to the $-I$-effect of the nitrogen atom. Finally, in the triphenylcarbonium cation there is a case of pure meta orientation due to concordant $-I$- and $-T$-effects.

Experimental Part

The conditions and results of the experiments on nitration of the borofluorides of onium compounds are presented in Table 1. The position of the nitro groups in the nitration products was determined by decomposition of the latter with pyridine, aqueous NaOH and $(CH_3)_2NH$, or thermally. All salts of trinitrotriphenyloxonium, trinitrotriphenylsulfonium, dinitrodiphenylbromonium, and dinitrodiphenylchloronium obtained for the first time in this work, their analyses and decomposition temperatures are given in Table 2.

Decomposition of $[(NO_2C_6H_4)_3O]BF_4$ **with alkali.**
a) A mixture of 0.56 g of trinitrotriphenyloxonium borofluoride (Table 1, expt. 1) and 15 ml of 20% NaOH solution was boiled for 2.5 hours. After the usual work-up, 0.4 g (91% of theory) of dinitrodiphenyl ether was isolated, m.p. 141.5–143° (m.p. of n,n'-dinitrodiphenyl ether 142–143° (8)), and a mixture of isomeric nitrophenols which, judging from the paper chromatogram (9), contains no m-isomer at all. b) Similar treatment of 0.3 g of trinitrotriphenyloxonium borofluoride obtained in experiment 2 (and likewise 3) gave 0.16 g of dinitrodiphenyl ether with m.p. 122–134°, which, judging from the UV spectrum, is a mixture of 95% n,n'-dinitrodiphenyl ether and 5% of the o,o'-isomer. On paper chromatograms of the mixture of nitrophenols isolated from the reaction there is no spot corresponding to m-nitrophenol.

Table 1

No. of experiments	Starting salt, g	Reagents, ml	Reaction conditions	Reaction product: formula	m.p., °C	yield, %	isomer ratio: meta, %	isomer ratio: para and ortho, %
1	$[(C_6H_5)_3O]BF_4$ 1	HNO_3 8.5 H_2SO_4 13.5	Sealed ampoule, 100°, 60 h	$[(NO_2C_6H_4)_3O]NO_3$ 0.25 g $[(NO_2C_6H_4)_3O]BF_4$ 0.83 g	126 216–217	82	not separated	almost 100% para
2	Same 0.33	NO_2BF_4 0.85 g CH_3NO_2 5	Shaking at room temp. 70 h	$[(NO_2C_6H_4)_3O]BF_4$ 0.92 g		41	Same	95% para 5% ortho

No. of experiments	Starting salt, g	Reagents,1 ml	Reaction conditions	Reaction product: formula	m.p., °C	yield, %	isomer ratio: meta, %	isomer ratio: para and ortho, %
3	Same 0.25 g	NO_2BF_4 1.0 g CH_3NO_2 5	Sealed ampoule, 100°, 23 h	$[(NO_2C_6H_4)_3O]BF_4$ 0.28 g	185–195	74	Same	Same
4	$[(C_6H_5)_3S]BF_4$ 1.15	HNO_3 7 H_2SO_4 19.0	Same 60 h	$[(NO_2C_6H_4)_3S]BF_4$ 1.40 g	221–225	72	Almost 100	Not separated
5	$[C_6H_5N(CH_3)_3]BF_4$ 1.86	HNO_3 7 H_2SO_4 15	Same 1.0	$[NO_2C_6H_4N(CH_3)_3]BF_4$ 1.20 g	185–187	86	96	4 para
6	$[(C_6H_5)_2Br]BF_4$ 1.25	HNO_3 5 H_2SO_4 21.0	Same	$[(NO_2C_6H_4)_2Br]NO_3$ 0.12 g $[(NO_2C_6H_4)_2Br]Br$ 1.17 g	109–110 95–95.5	91	94	6 para
7	Same 3.1	HNO_3 5.0 H_2SO_4 18	12 20°, 94 h	$[(NO_2C_6H_4)_2Br]Br$ 3.9 g	94–95	62	Almost 100	Not separated
8	$[(C_6H_5)_2Cl]BF_4$ 2.5	HNO_3 4 H_2SO_4 20	Same 7 1.5 h	$[(NO_2C_6H_4)_2Cl]_2PtCl_6$ 2.33 g	147–148	92	Almost 100	Not separated

1 In all experiments: HNO_3 ($d = 1.52$); H_2SO_4 ($d = 1.84$).

2 The reaction mixture was poured onto ice, neutralized with soda, and after separation the precipitate was treated with a saturated solution of $NaBF_4$ or $NaBr$ (exp. 6).

3 Prepared by the method of (7).

4 The reaction mixture was filtered from excess NO_2BF_4 and diluted with abs. ether.

5 The reaction mixture was poured onto ice and treated with a strong solution of $NaBF_4$ ($NaBr$ (exp. 7) or H_2PtCl_6 (exp. 8)) without prior neutralization of the excess acids.

6 The reaction mixture was poured onto ice, neutralized with soda, and treated with a conc. solution of NaJ.

Table 2

No.	Salt	m.p., °C	C, % found	C, % calculated	H, % found	H, % calculated	N, % found	N, % calculated
1	$[(n\text{-}NO_2C_6H_4)_3O]BF_4$	216-217	45.66 46.10	46.09	2.56 2.66	2.58	8.96 8.93	8.95
2	$[(n\text{-}NO_2C_6H_4)_3O]HgI_3$	159-160	22.68 22.53	22.44	1.44 1.40	1.26		
3	$[(n\text{-}NO_2C_6H_4)_3O]NO_3$	126-127	48.04 48.58	48.67	2.84 2.94	2.79	12.82	12.60
4	$[(n\text{-}NO_2C_6H_4)_3O][C_6H_2(NO_2)_3O]$	158-159	47.24 47.07	47.23	2.16 2.15	2.31	14.24	13.73
5	$[(n\text{-}NO_2C_6H_4)_3O]_2PtCl_6$	182-183	36.85 36.73	36.87	2.30 2.31	2.06		
6	$[(n\text{-}NO_2C_6H_4)_3O]B(C_6H_5)_4$	158-159	71.91 71.66	71.90	4.95 4.65	4.60	5.83 5.88	5.97
7	$[(m\text{-}NO_2C_6H_4)_3S]BF_4$	224-225	44.67 44.47	44.56	2.39 2.40	2.49	8.59 8.74	8.66
8	$[(m\text{-}NO_2C_6H_4)_3S]I$	194-195	41.35 41.38	41.17	2.39 2.34	2.30	8.18 8.12	8.00
9	$[(m\text{-}NO_2C_6H_4)_2Br]NO_3$	116-117	37.39 37.58	37.33	2.29 2.23	2.10	11.07 10.88	10.88
10	$[(m\text{-}NO_2C_6H_4)_2Br]Br$	94-95	35.43 35.42	35.67	1.98 1.96	2.00	6.68 6.61	6.93
11	$[(m\text{-}NO_2C_6H_4)_2Br]Cl$	98-100	40.00 40.02	40.07	2.43 2.43	2.25	8.06 7.84	7.79
12	$[(m\text{-}NO_2C_6H_4)_2Cl]HgBr_3$	123-124.5	20.30	20.02	1.20	1.12	3.98	3.89
13	$[(m\text{-}NO_2C_6H_4)_2Cl]_2PtCl_6$	147-148	29.64	29.80	1.90	1.67	6.02	5.79

Note. All the salts listed in Table 2, with the exception of the 3rd, 9th, and 11th, are poorly soluble in cold water; most of them are readily soluble in acetone, lower alcohols, and nitromethane; all the salts are insoluble in ether and hydrocarbons.

Decomposition of $[(NO_2C_6H_4)_3O]BF_4$ with dimethylamine. A mixture of 0.65 g of trinitrotriphenyloxonium fluoroborate (Table 1, experiment 1) and 10 ml of a 45% aqueous solution of $(CH_3)_2NH$ was left for 24 hours at room temperature. After the usual work-up, 0.34 g (94% of theory) of dinitrodiphenyl ether, m.p. 139-141°, and 0.07 g (31% of theory) of nitrodimethylaniline, m.p. 160.5-162° (m.p. of *p*-nitrodimethylaniline 161-162° (^{10})), were isolated.

Decomposition of $[(NO_2C_6H_4)_3O]BF_4$ with pyridine. A mixture of 0.7 g of trinitrotriphenyloxonium fluoroborate, obtained in experiment 1, and 5.5 ml of pyridine was boiled for 24 hours. After removal of the excess pyridine, 0.33

g (85% of theory) of n, n'-dinitrodiphenyl ether, m.p. 141-142°, was isolated.

Decomposition of $[(NO_2C_6H_4)_3S]BF_4$ **with alkali.** A mixture of 1.36 g of trinitrotriphenylsulfonium fluoroborate and 15 ml of a 10% NaOH solution was boiled for 25 hours. There was obtained 0.58 g (75% of theory) of crude m, m'-dinitrodiphenyl sulfide, identified by oxidation with CrO_3 in glacial acetic acid to the sulfone with m.p. 193-197° (m.p. of m, m'-dinitrodiphenyl sulfone 197° ([11])), and a mixture of nitrophenols which, judging from the paper chromatogram, was a mixture of m-nitrophenol and the p-isomer.

Decomposition of $[(NO_2C_6H_4)_3S]BF_4$ **with pyridine.** A mixture of 0.56 g of trinitrotriphenylsulfonium fluoroborate and 3 ml of pyridine was heated in a sealed ampoule for 3 hours to 225° and for a further 15 min at this temperature. After removal of the excess pyridine, 0.23 g (72% of theory) of m, m'-dinitrodiphenyl sulfide, m.p. 104.5-106.5°, was obtained; it was identified by oxidation to the sulfone with m.p. 197-199°.

Thermal decomposition of $[NO_2C_6H_4N(CH_3)_3]I$**.** 1.5 g of nitrophenyltrimethylammonium iodide was decomposed by heating in vacuo to 200°/5 mm. There was obtained 0.8 g (99% of theory) of a mixture of isomeric nitrodimethylanilines, from which 0.74 g of m-nitrodimethylaniline, m.p. 58.5-60.5° (m.p. of m-nitrodimethylaniline 59-60° ([12])), and 0.03 g of impure p-nitrodimethylaniline, m.p. 110-120°, were isolated by steam distillation.

Thermal decomposition of $[(NO_2C_6H_4)_2Br]Br$**.** a) Upon thermal decomposition of 0.5 g of dinitrodiphenylbromonium bromide, obtained in experiment 7, 0.42 g (84% of theory) of bromonitrobenzene with m.p. 54.5-55.5° was formed. A mixed sample with authentic m-nitrobromobenzene gave no depression of the melting point. b) Upon decomposition under the same conditions of 0.42 g of dinitrodiphenylbromonium bromide, obtained in experiment 6, 0.4 g (95% of theory) of bromonitrobenzene with m.p. 46-49° was formed. The UV spectrum of the substance showed that it was a mixture of 94% meta- and 6% para-isomers.

Decomposition of $[(NO_2C_6H_4)_2Cl]_2PtCl_6$ **with alkali.** A mixture of 0.46 g of dinitrodiphenylchloronium chloroplatinate and 15 ml of a 20% NaOH solution was left at room temperature for three days. The resulting mixture of nitrophenols, judging from the paper chromatogram, consisted mainly of m-nitrophenol with an admixture of p-nitrophenol.

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Note: Figure translations are in progress. See original paper for figures.