LI.—*The Relative Directive Powers of Groups of the Form* RO *and* RR′N *in Aromatic Substitution. Part III. The Nitration of some* p-*Alkyloxyanisoles.*

By Robert Robinson and John Charles Smith.

The nitration of quinol dialkyl ethers in cold acetic acid solution results in an almost theoretical yield of the pure mononitro-derivatives and the composition of the product can therefore be determined with considerable accuracy by the method of thermal analysis. Satisfactory methods for the preparation of 2-nitro-4-methoxyphenol and 3-nitro-4-methoxyphenol and of the ethyl, propyl, and *p*-nitrobenzyl ethers of each of these substances have been devised and the f. p.'s of mixtures of the isomeric pairs of nitroquinol dialkyl ethers have been determined. Examination of the products of nitration of quinol methyl ethyl ether, quinol methyl propyl ether, and quinol methyl *p*-nitrobenzyl ether with the aid of the diagrams so obtained shows that the directive powers of ethoxyl and propoxyl relative to methoxyl are higher than those observed in the catechol series, whilst the *p*-nitrobenzyloxy-group is weaker in the quinol than in the catechol series. Furthermore, whereas propoxyl is weaker than ethoxyl in the catechol series, it is now found to be stronger than ethoxyl in the quinol series. The theoretical implications of these results are discussed in the following communication.

EXPERIMENTAL.

2-*Nitro*-4-*methoxyphenol*.—The product (90% yield) of the action of nitric acid (1 mol.; *d* 1·42) on quinol dimethyl ether dissolved in acetic acid at 30° had m. p. 71·5° and was homogeneous (Mühlhauser, *Annalen*, 1881, **207**, 253, gives 71·5°, and Vermeulen, *Rec. trav. chim.*, 1905, **25**, 12, gives 72—73°, as the m. p. of nitroquinol dimethyl ether). After reduction and attempted condensation with phenanthraquinone, no phenazine could be obtained and consequently 2 : 3-dinitroquinol dimethyl ether, one of the products of the further nitration of nitroquinol dimethyl ether (Nietzki and Pechberg, *Ber.*, 1890, **23**, 1211), was not present. The nitrations examined quantitatively in the course of this work were conducted at a lower temperature and it may be safely concluded that no dinitro-derivatives were produced. Under the following conditions, the hydrolysis of nitroquinol dimethyl ether gives a 96% yield of recrystallised 2-nitro-4-methoxyphenol (compare Kauffmann and Fritz, *Ber.*, 1910, **43**, 1215; Pollecoff and Robinson, J., 1918, **113**, 647). A mixture of nitroquinol dimethyl ether (40 g.), sodium hydroxide (80 g.), and water (700 g.) was refluxed in a copper flask heated in an oil-bath for 54 hours, the liquid being agitated by means of a moderately rapid stream of air. Water (400 c.c.) was then added, the condenser removed, and boiling continued for 30 minutes or until the issuing steam condensed to clear drops on a test-tube filled with cold water. The mixture was cooled to about 60°, acidified with hydrochloric acid, and distilled in a current of steam. The product was collected, dried, and crystallised from light petroleum, separating in red prisms, m. p. 79—80°.

2-Nitro-4-methoxyphenol is also the product of the hydrolysis of nitroquinol dimethyl ether by means of hydrobromic acid. Combined with the fact that nitroveratrole under similar conditions gives 5-nitroguaiacol (Cardwell and Robinson, J., 1915, **107**, 255), this indicates the order $o > m > p$ for the influence of a nitro-group on the ease of hydrolysis of methoxyl by acids. A mixture of nitroquinol dimethyl ether (5 g.) and saturated aqueous hydrobromic acid (15 g.) was heated on the steam-bath for 6 hours. Subsequently 2-nitro-4-methoxyphenol (3·0 g.), m. p. 72—74° (recrystallised, m. p. 79—80°), and nitroquinol (0·5 g.), m. p. 132°, were isolated and identified. The theory of the hydrolysis of methoxyl groups by acids is necessarily complex. In the Friedel-Crafts reaction with phenol ethers the order of influence of the carbonyl group on the ease of hydrolysis of methoxyl is $o > p > m$. On the other hand, in euxanthone diethyl ether, we find $m > o$, in harmony with the nitroveratrole case. In contrast, the hydrolysis of phenolic ethers by alkaline solutions, as affected by the positions of groups like nitroxyl, gives uniform results—$o, p > m$.

Quinol Monomethyl Ether.—The method of Ullmann (*Annalen*, 1903, **327**, 116) for the semi-methylation of quinol was found to give poor yields and the following process was adopted after numerous trials. A solution of quinol (110 g.) in sodium hydroxide (100 g.) and water (700 c.c.), contained in a flask filled with hydrogen, was cooled to 12° and vigorously shaken after the addition of neutral methyl sulphate (120 c.c.) in one portion. After about 5 minutes the mixture was cooled and the dimethyl ether collected (33 g., m. p. 56°). The filtrate and washings were acidified with hydrochloric acid and cooled to about 8° for about 1 hour, thereafter the monomethyl ether was collected, washed with ice water, and dried (45 g., m. p. 52—54°). The aqueous solution was extracted with ether and the residue after evaporation of the solvent yielded to benzene a further 30 g. of less pure quinol monomethyl ether, m. p. 41—46°. For our purposes, it was necessary to ensure the absence of quinol from the product. The material was dissolved in benzene and any quinol which crystallised was separated; the solution was then distilled and a product, m. p. 53—54°, collected at 243—246°. This was redissolved in benzene, and the solution repeatedly shaken with small quantities of cold water. The ether was then again distilled, b. p. 243—244°, m. p. 56°. No coloration was developed in alkaline solution in contact with air. The substance crystallised from light petroleum has m. p. 56°, but when heated to about 200° and quickly cooled, the m. p. is 53°, changing in a week or two to 55°. Crystals, m. p. 56°, also change on keeping and the m. p. becomes 55°. Although these changes are small, the phenomenon is a real one.

Ethyl p-*Methoxyphenyl Carbonate.*—Ethyl chloroformate (95 c.c.) was added, with shaking and cooling in running water, to a solution of quinol monomethyl ether (124 g.) in water (300 c.c.) and sodium hydroxide (40 g.), and after 30 minutes the product was isolated by means of ether. The yield of a colourless, readily crystallising oil, b. p. 157°/17 mm., was 186 g. (93%). As traces of quinol monomethyl ether might have been produced in the distillation, the substance was washed with 0·05*N*-sodium hydroxide, dilute hydrochloric acid and water, and finally dried in a vacuum. The large, prismatic crystals had m. p. 21° (Found : C, 61·1 ; H, 6·2. $C_{10}H_{12}O_4$ requires C, 61·2 ; H, 6·2%). This ester is rather stable, 5 minutes' treatment with boiling 10% aqueous sodium hydroxide being necessary to effect complete solution.

Ethyl 3-*Nitro*-4-*methoxyphenyl Carbonate*, $OMe{\cdot}C_6H_3(NO_2){\cdot}O{\cdot}CO_2Et$.— Nitric acid (25 c.c.; *d* 1·52) was added to a solution of ethyl *p*-methoxyphenyl carbonate (25 g.) in acetic acid (25 c.c.), and the mixture heated on the steam-bath until the onset of a vigorous reaction manifested by the copious evolution of red fumes and a rise of temperature to 103°. After being maintained at 100° for 6 minutes, the liquid was cooled, water added, and the solid collected, washed, and dried (27·5 g. or 90%). The m. p. was 66°, and was raised only to 66·5° by crystallisation from light petroleum (Found : C, 49·7; H, 4·9; N, 5·9. $C_{10}H_{11}O_6N$ requires C, 49·8; H, 4·6; N, 5·8%). Slightly impure specimens are pale yellow and give a violet coloration with cold aqueous sodium hydroxide.

3-*Nitro*-4-*methoxyphenol.*—This substance, previously prepared by Klemenc (*Monatsh.*, 1914, **35**, 91) from its acetyl derivative, is best obtained in the following manner. A mixture of ethyl 3-nitro-4-methoxyphenyl carbonate (10 g.), sodium hydrogen carbonate (6 g.), methyl alcohol (17 c.c.), and water (17 c.c.) was boiled under reflux for 15 minutes, and the methyl alcohol then distilled from the solution. The cooled, red liquid was acidified with hydrochloric acid; the yellow oil obtained quickly crystallised (6·7 g. or 95%). The m. p. was 97—99°, and 98—100° after crystallisation from benzene. The substance is dimorphous and when melted and suddenly cooled it solidifies to an orange mass which in a few seconds changes with a crackling sound to yellow needles. In one experiment the temperature rose to 99°. The phenomenon is readily observed in a capillary tube and the unstable modification appeared to melt at about 85°. The potassium salt of this nitrophenol immediately after drying is violet and readily soluble in acetone but, when kept for some days or ground in a mortar, it becomes crimson and sparingly soluble, even in boiling acetone. The whole point of the method adopted for the preparation of this substance resides in the avoidance of the use of powerful alkaline reagents in the hydrolysis, since the methoxyl in the *o*-position to the nitro-group is readily attacked, and even by hot sodium carbonate to an extent which would vitiate our results.

3-*Nitro*-4-*ethoxyanisole*.—2-Nitro-4-methoxyphenol (10 g.) was treated in alcoholic solution with potassium ethoxide (from 2·34 g. of potassium), and after the solvent had been evaporated the red potassium salt was dried at 130° in a vacuum for 2 hours. It was then mixed with absolute alcohol (50 c.c.) and ethyl iodide (9 c.c.) and heated in a pressure bottle at 100° for 3 hours. The alcohol was removed by distillation and the product washed with successive quantities of 1% aqueous sodium hydroxide and with water, collected and dried (10·3 g. or 86%). The crude product had m. p. 38—39° and after crystallisation from methyl alcohol and from light petroleum the substance was obtained in short, yellow prisms, m. p. 39·5° and f. p. 39·0° after drying in a vacuum at 100° for 1 hour (Found: C, 54·6; H, 5·7; N, 7·2. $C_9H_{11}O_4N$ requires C, 54·8; H, 5·6; N, 7·1%).

2-*Nitro*-4-*ethoxyanisole*.—A solution of potassium ethoxide (from 1·95 g. of potassium) in alcohol * (15 c.c.) was added to one of 3-nitro-4-methoxyphenol (8·45 g.) in alcohol (20 c.c.), and after the introduction of ethyl iodide (5 c.c.) the mixture was boiled under reflux for 1 hour; the original deep red colour had then given place to orange. The isolation was like that of the isomeride described above and there resulted 9·5 g. (95%) of yellow needles, m. p. 36—38·5°. The purest specimens had m. p. 37—39°, f. p. 38·4°, and were obtained by crystallisation from methyl alcohol and light petroleum (Found: C, 54·7; H, 5·8; N, 7·1%). When quickly cooled from

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* In this case, the reaction is relatively facile and the use of ethyl alcohol is not disadvantageous. The ether was also prepared with methyl alcohol as the solvent.

100°, the substance melted sharply at 37°, but 1 hour later the m. p. was 37—39°.

Freezing Points of Mixtures of 3-*Nitro*-4-*ethoxyanisole and* 2-*Nitro*-4-*ethoxyanisole.*—Although these substances have a rapid rate of crystallisation, this is not the case with mixtures of them, especially near the eutectic, and the f. p.'s are ascertained only with great difficulty. In some examples the time taken to reach the maximum temperature after crystallisation had begun was no less than 20 minutes. Accurate standardisation of the procedure was therefore an urgent necessity. The external water-bath was contained in a Dewar vessel, and its temperature maintained 0·5° lower than that of the mixture. The mixture was supercooled 1·5°, nucleated from a trace of solid left on the thermometer stem, and stirred at the rate of 1 revolution per second. The temperature could be estimated to the nearest 0·02°. The eutectic could not be accurately located, since in this region a double f. p. was observed. The following mean values were selected, the first number of each pair indicating the percentage of 3-nitro-4-ethoxyanisole in the mixture: 0·0, 38·4°; 7·8, 34·7°; 18·2, 28·0°; 25·4, 24·35°; 31·6, 21·25°; 38·1, 17·5°; 40·75, 15·9°; 41·5, 14·15°; 43·1, 14·5°; 45·9, 12·1° (14·2°); 48·0, 11·8° (14·1°); 50·6, 13·9°; 57·6, 19·1°; 63·3, 22·3°; 67·8, 24·7°; 68·5, 25·2°; 75·7, 28·8°; 81·0, 31·1°; 84·3, 32·3°; 94·1, 36·3°; 100·0, 39·0°.

As a confirmation a mixture was made of 3-nitro-4-ethoxyanisole (1·0643 g.) and 2-nitro-4-ethoxyanisole (0·6413 g.) and found to freeze at 21·9°. From the graph, 21·9° corresponds to 62·4% of the 3-nitro-isomeride (calc., 62·4%).

Nitration of 4-*Ethoxyanisole.*—Fiala (*Monatsh.*, 1884, **5**, 233) has prepared 4-ethoxyanisole and states that its m. p. is 39°. Using pure quinol monomethyl ether and ethyl iodide, b. p. 72·4°, we find that the crystallised product has m. p. 36—37°, b. p. 216—217°/754 mm. (Found: C, 70·9; H, 8·0. Calc.: C, 71·0; H, 8·0%). The nitric acid employed in the nitrations described in this communication had *d* 1·42 and was distilled and freed from oxides of nitrogen by means of a current of air. The acetic acid also was purified and froze at 16°. A mixture of acetic acid (3 c.c.) and nitric acid (1·77 g.; 1 mol.) was gradually introduced by means of a capillary tube below the surface of a stirred solution of 4-ethoxyanisole (2·91 g.; 1 mol.) in acetic acid (6 c.c.) cooled to 4°. As no change of colour occurred, the temperature was allowed to rise to 6° after about 10% of the acid had been added. A yellow colour developed and the mixture was then cooled to 0—1° and the remainder of the nitric acid added during 20 minutes, after which stirring and cooling at 0° were maintained for 20 minutes. The temperature was then allowed to reach 10° for 5 minutes. A further molecular proportion of nitric acid dissolved in acetic acid (1·5 c.c.) was introduced with similar precautions, and the mixture at 0° was then diluted with water (60 c.c.) at 2°. After being stirred for a few minutes, the mixture was kept for an hour. The oil had solidified and the clear supernatant liquid could be siphoned away without loss of the product. The material was then washed successively with water (20 c.c.) at 30°, twice with very weak aqueous sodium bicarbonate (10 c.c.) at 30°, and finally thrice with water at 30°. In each case stirring was resorted to and the washings were removed after solidification of the oil by cooling to about 5°. After drying to constant weight (3·565 g., 94·6%) in a vacuum, the specimen (*a*) was prepared for determination of the f. p. by heating in a vacuum at 100° for 30 minutes (Found: N, 7·2. Calc.: N, 7·1%). Further nitrations of 5 g. of 4-ethoxyanisole in an identical fashion gave 6·28 g. (*b*; 97%) and 6·23 g. (*c*; 96%) of the mixed isomerides.

The results of analysis are set out in the following table.

Specimen.	Grams of mixture taken.	Weight of 3-nitro-isomeride added.	F. p.	% of 3-nitro-isomeride indicated.	% of 3-nitro-isomeride in the nitration product.
(*a*) 1	2·6640	0	21·8°	62·2	62·2
2	—	1·4448	28·6	75·5	62·1
(*b*) 1	3·6087	0	21·95	62·4	62·4
2	—	1·5058	27·7	73·5	62·4
3	2·4048 of last mixture, f. p. 27·7°	2·2597	33·5	86·5	62·9
(*c*) 1	3·2733	0	21·9	62·4	62·4
2	—	0·9945	26·4	70·9	62·1
3	—	1·6532	28·4	75·0	62·4
					Mean 62·36

In order to ascertain what change of composition, if any, was entailed in the isolation processes, a mixture of the isomerides, f. p. 23·2°, was dissolved in the appropriate quantities of nitric and acetic acids so as to imitate the result of an actual nitration. Isolation and washing were carried out as described above, but before drying the whole series of operations was repeated. The dried material then froze at 23·4°. Two such treatments therefore only change the f. p. by 0·2° and if it is assumed that one isolation process raises the f. p. by 0·1°, the corrected composition of the product of nitration is 62·2% of the 3-nitro-isomeride and 37·8% of the 2-nitro-isomeride. Hence the directive power of ethoxyl relative to methoxyl (100) is 163 in the quinol series.

3-*Nitro*-4-*propoxyanisole*, $OMe\cdot C_6H_3(NO_2)\cdot OPr^{\alpha}$.—The propyl iodide employed in the preparation of this substance and of its isomeride had b. p. 101·2—101·7° (Found: I, 74·7, 74·7. Calc.:

I, 74·7%), and the propyl alcohol also was fractionated—b. p. 96·9—97·9°.

A mixture of 2-nitro-4-methoxyphenol (16·9 g.), potassium propoxide (from 3·85 g. of potassium), propyl iodide (20 c.c.), and propyl alcohol (50 c.c.) was boiled under reflux for 11 hours. The solvent was then removed in a vacuum at 100°, and the residue yielded to ether 10 g. (48%) of a dark brown liquid, m. p. 10·22°. This boiled at 127° under less than 1 mm. pressure and the clear yellow distillate had m. p. 10·35°. Repeated crystallisation from methyl alcohol at —15° raised the m. p. to the constant value of 10·7° (Found : C, 56·9; H, 6·4; N, 6·6. $C_{10}H_{13}O_4N$ requires C, 56·9; H, 6·2; N, 6·6%). In a second experiment, exactly the same results were obtained.

Attempts to improve the above process by employing the silver salt of the nitrophenol in place of the potassium salt were wholly unsuccessful. The silver salt of 2-nitro-4-methoxyphenol was prepared from the sodium salt and silver nitrate in aqueous solution. The material was dried in a vacuum (Found : Ag, 39·4. $C_7H_8O_4NAg$ requires Ag, 39·1%) and was remarkably stable towards alkyl iodides. Boiling methyl and ethyl iodides produced no effect in 10 minutes, and the action of boiling propyl iodide alone for 12 hours or in solution in ether, benzene, ethyl acetate, methyl, ethyl or propyl alcohol also gave negative results or very poor results.

2-*Nitro*-4-*propoxyanisole*.—This ether was obtained in 85% yield by the usual method applied to a methyl-alcoholic solution boiling during 12 hours. In all such processes the solvent chosen should be such that alcoholysis of alkyloxy-groups in the *o*- or *p*-positions to nitroxyl cannot introduce impurities. The pure substance, crystallised from methyl alcohol and from light petroleum, has f. p. 32·0° (31·98° in a second preparation) (Found : C, 57·0; H, 6·4; N, 6·7%).

Mixtures of 3-*Nitro*-4-*propoxyanisole and* 2-*Nitro*-4-*propoxyanisole*.—The following values of the f. p.'s were employed for the construction of a graph, and the first number of each pair indicates the percentage of 2-nitro-4-propoxyanisole in the mixture : 100·0, 32·0°; 95·9, 30·55°; 92·6, 29·5°; 86·5, 27·45°; 80·5, 25·1°; 74·9, 22·9°; 68·6, 20·2°; 63·7, 18·0°; 57·5, 15·0°; 53·1, 12·8°; 48·0, 10·35°. The readings for the mixtures containing less than 48% of the 2-nitro-isomeride were too indefinite to be of practical value.

Nitration of 4-*Propoxyanisole*.—4-Propoxyanisole (Fiala, *Monatsh.*, 1884, **5**, 234) was obtained in 85% yield in the usual manner and has b. p. 135°/15 mm. and m. p. 26—27°. The nitration was carried out in precisely the same way as that of 4-ethoxyanisole but, as the product was a liquid at 0°, it was necessary after the washings to await the complete settling of the droplets before removing the supernatant fluid. The washed product was siphoned with the aid of methyl alcohol through a Pregl micro-filter into a weighed tube, and the methyl alcohol and water were removed by a current of filtered air at 50° and finally at 110° in a vacuum. In two experiments (*a*) and (*b*) the yields were 97% and 98%, respectively [Found in (*a*): N, 6·7. Calc.: N, 6·6%]. The results of the analysis are tabulated below.

Specimen.	Grams of nitration product.	Weight of 2-nitro-isomeride added.	F. p.	% of 2-nitro-isomeride indicated.	% of 3-nitro-isomeride in the nitration product.
(*a*) 1	1·1478	0·6043	15·1°	58·0	64·1
2	—	1·0971	19·5	67·1	64·3
3	—	1·6141	22·25	73·2	64·5
(*b*) 1	1·0771	0·6128	15·6	58·9	64·5
2	—	0·9326	18·85	65·6	64·2
3	—	1·2782	21·05	70·5	64·5
					Mean 64·35

As a check the following experiment was carried out. A mixture of 2-nitro-4-propoxyanisole (1·5173 g.) and 3-nitro-4-propoxyanisole (0·5560 g.) containing 73·2% of the former isomeride was made and this was found to have f. p. 22·25°, agreeing with the value read from the graph. This mixture (0·6 g.) added to that (*a* 3) of the same f. p. mentioned in the above table (1·0 g.) gave a product, f.p. 22·25°.

Corresponding to the above results, the directive power of the *n*-propoxy-group in the quinol series is 180.

3-*Nitro*-4-p-*nitrobenzyloxyanisole*.—2-Nitro-4-methoxyphenol (1·06 mols.), potassium propoxide (1·04 mols.), and *p*-nitrobenzyl bromide (1 mol.) were employed in the preparation of this substance in boiling propyl-alcoholic solution. The yield was 98% of the theoretical calculated on the *p*-nitrobenzyl bromide employed. The substance crystallises from benzene in yellow needles, m. p. 153°, f. p. 152·8° (Found: C, 55·3; H, 4·0; N, 9·2. $C_{14}H_{12}O_6N_2$ requires C, 55·2; H, 4·0; N, 9·2%).

2-*Nitro*-4-p-*nitrobenzyloxyanisole* was prepared in the usual manner in methyl-alcoholic solution and the yield was 96%. After recrystallisation from benzene, the substance was heated at 100° for an hour; it then melted at 120—125° with sudden evolution of benzene. After heating in a vacuum at 130—135° for 30 minutes in a slow current of air, the substance melted at 123·5° and froze at 123·0° (Found: C, 55·3; H, 4·3; N, 9·2%). The compound is more sparingly soluble in benzene than its less fusible isomeride.

Mixtures of 3-*Nitro*-4-p-*nitrobenzyloxyanisole and* 2-*Nitro*-4-p-*nitrobenzyloxyanisole*.—The outer bath of the cryometer was a large beaker of sulphuric acid. The following values of the f. p. were employed in the analysis below and the first number of each pair represents the percentage of 2-nitro-4-*p*-nitrobenzyloxyanisole in the mixture : 100·0, 123·0°; 93·9, 120·25°; 87·9, 117·5°; 83·65, 115·65°; 78·2, 112·95°. The corresponding curve is almost a straight line. Nearer to the eutectic it was not found possible to obtain concordant readings, but the following mean values indicate the form of the curve : 74·25, 111·5°; 70·2, 109·9°; 67·6, 109·0°; 66·7, 108·4°; 59·8, 111·6°; 55·7, 114·4°; 49·4, 123·0°.

4-p-*Nitrobenzyloxyanisole.*—*p*-Methoxyphenol (1·05 mols.), potassium hydroxide (1·02 mols.), and *p*-nitrobenzyl bromide (1 mol.) in boiling methyl-alcoholic solution gave a 95% yield of the ether. The substance is sparingly soluble in cold methyl or ethyl alcohol, readily soluble in benzene, and crystallises from ethyl alcohol in large, yellow prisms, m. p. 87·5° (Found : C, 64·7; H, 5·1; N, 5·4. $C_{14}H_{13}O_4N$ requires C, 64·8; H, 5·1; N, 5·4%).

In view of the interest which has been evinced in regard to the bright yellow colour of nitroquinol dimethyl ether, it should be noted that this quinol methyl *p*-nitrobenzyl ether is more intensely coloured than either of the nitroquinol methyl *p*-nitrobenzyl ethers. This clearly indicates that the colour of nitroquinol dimethyl ether is due, not to any quinonoid rearrangement, but to the interaction of the *p*-dialkyloxybenzene nucleus and the nitroxyl functioning independently. The direct attachment of the nitro-group to the quinol nucleus depresses its reactivity and should have a bathochromic effect.

Nitration of 4-p-*Nitrobenzyloxyanisole.*—A mixture of acetic acid (12 c.c.) and nitric acid (12 c.c.; *d* 1·42) was added in one portion to a well-stirred solution of 4-*p*-nitrobenzyloxyanisole (3·0 g.) in acetic acid (30 c.c.). The temperature remained at 22° for 30 seconds, then rose to 25°, and the product began to crystallise. Water (150 c.c.) was added after 15 minutes, and the solid collected after 30 minutes and washed with water. The material (*a*) was dried at 80—90° for 10 hours and then weighed 3·45 g. (98%) (Found : N, 9·3. Calc. : N, 9·2%). A second specimen (*b*) was similarly obtained by nitration at 15—20° in 99% yield, and a third (*c*) by nitration at 16—21° in 99% yield.

Specimen.	Weight of nitration product.	Weight of 2-nitro-isomeride added.	F. p.	% of 2-nitro-isomeride indicated.	% of 2-nitro-isomeride in nitration product.
(*a*, *b*, *c*)	—	—	(109—110·5°)	—	(68—72·5)
(*a*)	0·7201	0·8143	117·2°	87·1	72·5
	—	1·4556	119·0	91·0	72·8
(*b*)	1·1561	0·9747	116·25	85·2	72·7
	—	1·7854	118·1	89·2	72·5
(*c*)	1·0287	0·8636	116·0	84·6	71·7
				Mean	72·4

A mixture of 2-nitro-4-*p*-nitrobenzyloxyanisole (0·9930 g.) and 3-nitro-4-*p*-nitrobenzyloxyanisole (0·1808 g.) contains 84·6% of the 2-nitro-isomeride and has f. p. 116·0°, confirming the graph in that region. When 1·17 g. of this mixture was added to 1·4 g. of the mixture (from *c*) given in the above table as of f. p. 116·0°, the f. p. was 116·0°. From the above data it appears that the directive power of the *p*-nitrobenzyloxy-group in the quinol series is 38.

An error of 0·1° in the f. p. causes an error of 0·2 in the percentage obtained from the graph and one of 0·4 in the calculated percentage composition of the mixture. In the case of ethoxyl an error of 0·1° in the f. p. produces an error of 0·27—0·3 in the calculated percentage composition of the nitration product, and in the case of propoxyl an error of 0·1° in the f. p. would cause an error of 0·24 in the percentage composition read from the graph and an error of 0·5 in the calculated percentage composition of the nitration product.

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