

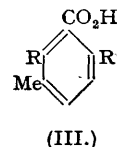
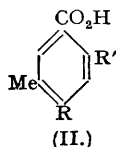
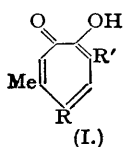
### 459. Purpurogallin. Part VIII.\* Nitration and Nitrosation of $\beta$ -Methyltropolone.

By ROBERT D. HAWORTH and PHILLIP R. JEFFERIES.

Nitrosation of  $\beta$ -methyltropolone gives a  $\gamma$ -nitroso-derivative, and nitration yields a mixture of  $\gamma$ -,  $\alpha$ -, and  $\alpha'$ -nitro-compounds, with the first predominating. The structure of the nitro-compounds has been established by rearrangement in the presence of alkalis to nitro-*m*-toluic acids. Reduction to the  $\gamma$ -,  $\alpha$ -, and  $\alpha'$ -amines has been examined, and the  $\gamma$ -amine was identical with the amine obtained (see Part IV) by reduction of *p*-tolyl-azo- $\beta$ -methyltropolone, thus proving that diazo-coupling occurs in the  $\gamma$ -position in  $\beta$ -methyltropolone. The  $\alpha$ - and  $\alpha'$ -amino-tropolones gave diazo-compounds, but when warmed with dilute sulphuric acid the solutions of these compounds, instead of yielding the  $\alpha$ - and  $\alpha'$ -hydroxytropolones, underwent ring contraction and rearrangement and gave 6- and 4-methyl-salicylic acid, respectively. The mechanism of the rearrangement is discussed.

In a recent paper, Doering and Knox (*J. Amer. Chem. Soc.*, 1951, **73**, 828) describe the preparation of a nitro- and a nitroso-tropolone, and we now record some of our results concerning substitution in  $\beta$ -methyltropolone. A preliminary report on some of this work has been described elsewhere (*Chem. and Ind.*, 1950, 841).

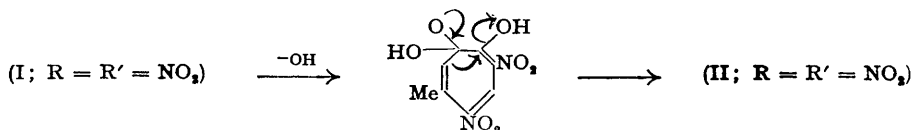
We have examined nitration and nitrosation of  $\beta$ -methyltropolone (I; R = R' = H), and although oxidation played a prominent rôle, by nitration in acetic acid at 0°, molar quantities of nitric acid being used, we were able to isolate three mononitro- $\beta$ -methyltropolones, m. p. 176—177°, 146—147°, and 206°, severally, together with a small quantity of a carboxylic acid, m. p. 172—173°, which was found to be 4 : 6-dinitro-*m*-toluic acid (II; R = R' = NO<sub>2</sub>) by comparison with a sample prepared from 4 : 6-dinitro-*m*-xylene (Errera and Maltese, *Gazzetta*, 1903, **33**, II, 278). The formation of (II; R = R' = NO<sub>2</sub>) must have been due to a benzylic



acid type rearrangement of  $\beta$ -methyl- $\alpha'\gamma$ -dinitrotropolone (I; R = R' = NO<sub>2</sub>) either during the reaction or in the process of isolation. Nozoe's observation (for references, see Part IV, *J.*, 1951,

\* Part VII, *J.*, 1951, 1325.

561) that dinitrohinokitiol rearranges to a dinitroisopropylbenzoic acid when warmed with water, and the results reported below illustrate the marked influence of nitro-substituents in accelerating the benzilic acid type changes in the tropolones; the effect is in accordance with the polar nature of the nitro-group which increases the attraction for the hydroxyl ion necessary for the transformation



The bulk (60%) of the  $\beta$ -methylnitrotropolone mixture consisted of  $\beta$ -methyl- $\gamma$ -nitrotropolone (I; R = NO<sub>2</sub>, R' = H), m. p. 176—177°, which underwent a benzilic acid type rearrangement when warmed with 2N-sodium hydroxide. The acidic product, m. p. 214—215°, was shown to be 6-nitro-*m*-toluic acid (II; R = NO<sub>2</sub>, R' = H) by comparison with an authentic sample obtained by oxidation of 4-nitro-*m*-xylene (Beilstein and Kreusler, *Annalen*, 1867, **144**, 168; Muller, *Ber.*, 1909, **42**, 430). The orientation of  $\beta$ -methyl- $\alpha'$ -nitrotropolone (I; R = H, R' = NO<sub>2</sub>), m. p. 146—147°, obtained in 14% yield, was established similarly by conversion into 4-nitro-*m*-toluic acid, m. p. 132—133°, identified by comparison with a sample obtained by nitration of *m*-toluic acid (Finkeldee, *Ber.*, 1905, **38**, 3542; Muller, *loc. cit.*). The  $\beta$ -methyl- $\alpha$ -nitrotropolone (IV; R = NO<sub>2</sub>), m. p. 206°, isolated in 8% yield, was more stable to alkali than the isomers, but short warming with 30% sodium hydroxide gave an excellent yield of an acid, m. p. 218—219°, identical with 2-nitro-*m*-toluic acid (III; R = NO<sub>2</sub>, R' = H) (Muller, *loc. cit.*).



Reduction of  $\beta$ -methyl- $\gamma$ -nitrotropolone (I; R = NO<sub>2</sub>, R' = H) with sodium dithionite gave  $\gamma$ -amino- $\beta$ -methyltropolone (I; R = NH<sub>2</sub>, R' = H), m. p. 224° (decomp.), which yielded a benzylidene derivative, m. p. 145—146°.  $\gamma$ -Amino- $\beta$ -methyltropolone was found to be identical with the amine prepared (Part IV, *loc. cit.*) by reductive fission of *p*-tolylazo- $\beta$ -methyltropolone. Hence, diazo-coupling must have occurred in the  $\gamma$ -position of the tropolone nucleus, and the hydroxy-compound prepared from this amine as in Part IV must be  $\gamma$ -hydroxy- $\beta$ -methyltropolone (I; R = OH, R' = H). The aromatic character of the  $\gamma$ -amino-group is also shown by decomposition of the diazonium sulphate with potassium iodide, whereby  $\gamma$ -iodo- $\beta$ -methyltropolone (I; R = I, R' = H), m. p. 169—170°, was obtained.

Treatment of  $\beta$ -methyltropolone with nitrous acid gave  $\beta$ -methyl- $\gamma$ -nitrosotropolone (I; R = NO, R' = H), m. p. 178° (decomp.), the structure of which was established by reduction in the presence of a palladium catalyst, 2 moles of hydrogen being absorbed and  $\gamma$ -amino- $\beta$ -methyltropolone (I; R = NH<sub>2</sub>, R' = H) obtained.

In the presence of a palladium catalyst, hydrogen readily reduced  $\beta$ -methyl- $\alpha'$ -nitrotropolone to  $\alpha'$ -amino- $\beta$ -methyltropolone (I; R = H, R' = NH<sub>2</sub>), m. p. 136—137°, and in the same way  $\beta$ -methyl- $\alpha$ -nitrotropolone gave  $\alpha$ -amino- $\beta$ -methyltropolone (IV; R = NH<sub>2</sub>), m. p. 151°. Both these new amines, like the previously described  $\gamma$ -isomer, are yellow compounds which show characteristic tropolone ultra-violet absorption spectra (p. 2071). The  $\alpha$ - and  $\alpha'$ -amines react with nitrous acid very readily at 0° to give highly coloured diazonium solutions from which we had hoped to prepare the corresponding hydroxytropolones by the method described in Part IV for  $\gamma$ -hydroxy- $\beta$ -methyltropolone. The products from  $\alpha$ - and  $\alpha'$ -amines, which were obtained in high yield, gave violet ferric tests reminiscent of salicylic acid, and the ultra-violet absorption spectra indicated in both cases that the compounds were benzenoid and that the tropolone ring was absent. The substance obtained from  $\alpha$ -amino- $\beta$ -methyltropolone was shown to be identical with a specimen of 6-methylsalicylic acid (V; R = H, R' = Me) prepared from 6-methylanthranilic acid (Gabriel and Thieme, *Ber.*, 1919, **52**, 1079; Mayer and Schulze, *Ber.*, 1925, **58**, 1469), and the acid obtained from  $\alpha'$ -amino- $\beta$ -methyltropolone was shown to be 4-methylsalicylic acid (V; R = Me, R' = H), m. p. 177° (Tiemann and Schotten, *Ber.*, 1878, **11**, 777; Duff, *J.*, 1941, 547). It is unlikely that the ring contractions occur during the reactions of nitrous acid with the  $\alpha$ - and  $\alpha'$ -aminotropolones because the resultant red solutions have the properties of diazonium solutions and couple with alkaline  $\beta$ -naphthol. It is equally improbable

that the diazo-group is replaced by hydroxyl during the reaction because  $\alpha$ - and  $\alpha'$ -hydroxytropolones are quite stable in the presence of hot dilute acids: for example, puberulonic acid is decarboxylated to puberulic acid by being boiled with 2N-sulphuric acid (Corbett, Hassell, Johnson, and Todd, *J.*, 1950, 4). The most probable explanation\* of these ring contractions is that they occur simultaneously with the elimination of nitrogen from the diazonium salts by a mechanism which is illustrated below for the transformation in the case of  $\alpha'$ -amino- $\beta$ -methyltropolone, and a similar scheme may be advanced for the corresponding  $\alpha$ -amine.



On the other hand, an application of this mechanism to the case of  $\gamma$ -amino- $\beta$ -methyltropolone would require the formation of  $\beta$ -(2-hydroxy-4-methylcyclobuta-1:3-dienyl)acrylic acid, and replacement of the diazonium group by hydroxyl with the production of  $\gamma$ -hydroxy- $\beta$ -methyltropolone as described in Part IV (*loc. cit.*) would obviously meet with less resistance.

#### EXPERIMENTAL.

$\beta$ -Methyltropolone was prepared from purpurogallin *via*  $\beta$ -carbomethoxy- $\alpha$ -carboxytropolone by the method described in Part IV (*loc. cit.*).

**Nitration of  $\beta$ -Methyltropolone.**—Preliminary experiments showed that the reaction was complex and accompanied by considerable oxidation, but by working in cold acetic acid solution at 0° satisfactory results were obtained.  $\beta$ -Methyltropolone (0.5 g.) in glacial acetic acid (2.5 ml.) was cooled in ice, and nitric acid (0.25 ml.;  $d_4^{20}$  1.41) added with agitation. An orange colour developed, and after 30 minutes at 0° the precipitate was removed and washed with water. The material obtained from ten such runs was fractionally crystallised from alcohol to give (a) long prisms of  $\beta$ -methyl- $\gamma$ -nitrotropolone (I; R = NO<sub>2</sub>, R' = H) (2.0 g.), m. p. 176–177°, which for analysis were sublimed at 130°/11 mm. (Found: C, 52.8; H, 3.9; N, 8.1. C<sub>8</sub>H<sub>7</sub>O<sub>4</sub>N requires C, 53.0; H, 3.9; N, 7.7%), and (b) prisms of  $\beta$ -methyl- $\alpha$ -nitrotropolone (IV; R = NO<sub>2</sub>) (0.4 g.), m. p. 206° (Found: C, 52.5; H, 4.1; N, 7.4%). The acetic acid filtrate was diluted with water (200 ml.), and the precipitate (0.5 g.) (A) separated. The filtrate was extracted with chloroform (4 × 100 ml.) and washed with sodium hydrogen carbonate solution, the organic layer dried, and the solvent removed. From the tarry residue  $\beta$ -methyltropolone (0.6 g.) was recovered by extraction with hot light petroleum (b. p. 60–80°), but the residual amorphous residue did not yield any further crystalline material. On acidification the sodium hydrogen carbonate washings yielded a precipitate (0.4 g.) (B) which was removed, and the filtrate on extraction with chloroform and evaporation of the dried extract gave a residue which deposited crystals (0.2 g.) (C) from the minimum volume of boiling alcohol. The mother-liquor was precipitated with water, and after solidification the precipitate (0.25 g.) was removed and crystallised from benzene (charcoal); elongated plates of 4:6-dinitro-*m*-toluic acid, m. p. 172–173° (Found: C, 42.6; H, 3.0; N, 12.4%; equiv., 229. Calc. for C<sub>8</sub>H<sub>6</sub>O<sub>6</sub>N<sub>2</sub>: C, 42.5; H, 2.7; N, 12.4%; equiv., 226), were obtained and identified by comparison with an authentic sample prepared by oxidation of 4:6-dinitro-*m*-xylene (Errera and Maltese, *loc. cit.*). Excess of ethereal diazomethane gave the methyl ester, m. p. 105° (Found: C, 45.3; H, 3.7. C<sub>9</sub>H<sub>8</sub>O<sub>6</sub>N<sub>2</sub> requires C, 45.0; H, 3.4%). The materials (A), (B), and (C) were mixtures, and fractional crystallisation from alcohol yielded yellow plates of  $\beta$ -methyl- $\alpha'$ -nitrotropolone (I; R = H, R' = NO<sub>2</sub>) (0.7 g.), m. p. 146–147° (Found: C, 53.2; H, 4.0; N, 7.7%), and a further crop of  $\beta$ -methyl- $\alpha$ -nitrotropolone (0.15 g.).

The three mononitro- $\beta$ -methyltropolones gave a red-green colour with alcoholic ferric chloride and slowly dissolved in sodium hydrogen carbonate to give orange solutions.

**Alkaline Rearrangement of  $\beta$ -Methyl- $\gamma$ -nitrotropolone.**—Unchanged material was recovered after boiling the nitro-compound with aqueous sodium carbonate or 2N-sulphuric acid.  $\beta$ -Methyl- $\gamma$ -nitrotropolone (0.2 g.) was refluxed with 2N-sodium hydroxide (3 ml.) for 1 hour. The dark solution was acidified with 2N-sulphuric acid, and the suspension extracted with ether (3 × 20 ml.). Evaporation of the dried extract gave an amorphous residue which was purified by sublimation at 120°/8 mm. Crystallisation from 50% aqueous alcohol gave long prisms of 6-nitro-*m*-toluic acid (0.05 g.), m. p. 214–215° (Found: equiv., 175. Calc. for C<sub>8</sub>H<sub>7</sub>O<sub>4</sub>N: equiv., 181), alone or mixed with an authentic sample prepared by oxidation of 4-nitro-*m*-xylene (Beilstein and Kreisler, *loc. cit.*; Muller, *loc. cit.*). Comparison of samples of the methyl ester, m. p. 81–82° (Herre, *Ber.*, 1895, 28, 597), confirmed the identity.

**Alkaline Rearrangement of  $\beta$ -Methyl- $\alpha'$ -nitrotropolone.**—The nitro-compound (0.2 g.) was heated under reflux with 2N-sodium hydroxide (3 ml.) for 30 minutes. The cooled dark solution was acidified with 2N-sulphuric acid, the suspension extracted with ether (3 × 25 ml.) which was washed with sodium

\* When this manuscript was completed a brief statement of some recent observations by Nozoe and his co-workers came to hand (*J. Amer. Chem. Soc.*, 1951, 73, 1895). The conversion of  $\alpha$ - and  $\alpha'$ -aminohinokitiol into 6- and 4-isopropylsalicylic acids, respectively, is described, and a mechanism similar to that proposed above is suggested.

hydrogen carbonate solution, and the acidic material recovered, isolated with ether, and sublimed at 130°/10 mm. The colourless sublimate (0.041 g.) was crystallised first from benzene, then from water, to give needles of 4-nitro-*m*-toluic acid, m. p. 132—133°, alone or mixed with an authentic sample obtained by nitration of *m*-toluic acid (Muller, *loc. cit.*; Finkeldee, *loc. cit.*). The methyl ester, prepared with an excess of ethereal diazomethane, had m. p. 78—79°, alone or mixed with methyl 4-nitro-*m*-toluate (Jurgens, *Ber.*, 1907, **40**, 4411).

**Alkaline Rearrangement of  $\beta$ -Methyl- $\alpha$ -nitrotropolone.**—This substance was scarcely affected by the above treatment with 2N-sodium hydroxide, and alkali fusion at 140—150° produced only amorphous material. The nitrotropolone (0.3 g.) was refluxed with 30% sodium hydroxide solution for 10 minutes. Acidification of the cooled solution gave a clean precipitate which was extracted with ether and recovered by washing it with sodium hydrogen carbonate and acidification. The product (0.22 g.) after two crystallisations from 50% aqueous alcohol yielded 2-nitro-*m*-toluic acid, m. p. 218—219° (Found: equiv., 179. Calc. for  $C_8H_7O_4N$ : equiv., 181), undepressed by admixture with an authentic sample, m. p. 219—220°, obtained by nitration of *m*-toluic acid (Muller, *loc. cit.*). The methyl ester, prepared with an excess of ethereal diazomethane, had m. p. 72—73°, alone or mixed with a sample of methyl 2-nitro-*m*-toluate (Muller, *loc. cit.*).

**$\gamma$ -Amino- $\beta$ -methyltropolone** (I; R = NH<sub>2</sub>, R' = H).— $\beta$ -Methyl- $\gamma$ -nitrotropolone (0.2 g.) was suspended in water (10 ml.) and treated with 10% aqueous sodium dithionite (10 ml.) containing 2N-sodium hydroxide (1 ml.). The colour of the solution changed fairly quickly from orange to light yellow. The solution was acidified with dilute hydrochloric acid, made slightly alkaline with ammonia solution, and acidified with a little acetic acid. Repeated extraction with ethyl methyl ketone gave, on distillation of the dried extract, a yellow residue (0.18 g.), which was sublimed at 190°/0.5 mm. Crystallisation from alcohol gave yellow prisms of  $\gamma$ -amino- $\beta$ -methyltropolone, m. p. 224° (decomp.) (Found: C, 63.2; H, 6.0; N, 9.4. Calc. for  $C_8H_9O_2N$ : C, 63.5; H, 6.0; N, 9.3%), alone or mixed with a sample of amine prepared from *p*-tolylazo- $\beta$ -methyltropolone by the method described in Part IV (*loc. cit.*). The identity was confirmed by the preparation, in alcoholic solution, of a *benzylidene* derivative, m. p. 145—146° (Found: C, 74.9; H, 5.5; N, 6.0.  $C_{15}H_{13}O_2N$  requires C, 75.3; H, 5.5; N, 5.9%), which gives a purple ferric test.

**$\gamma$ -Iodo- $\beta$ -methyltropolone** (I; R = I, R' = H).—The above amino-compound (0.27 g.) in water (5 ml.) and sulphuric acid (0.4 ml.) was cooled to 10° and diazotised by gradual addition of sodium nitrite (0.13 g.) in water (2 ml.), an orange solution being obtained. Decomposition was brought about by addition to potassium iodide (2 g.) in water (5 ml.) and gentle heating, followed by 5 minutes' boiling. The cooled suspension was extracted with ether, and the extract washed with sodium thio-sulphate solution, dried, and evaporated. Repeated extraction of the residue with *cyclohexane* gave  $\gamma$ -iodo- $\beta$ -methyltropolone, which separated from acetone in cream plates (0.219 g.), m. p. 169—170° (Found: C, 37.1; H, 2.7; I, 48.2.  $C_8H_7O_2I$  requires C, 36.7; H, 2.5; I, 48.5%); it gives a green colour with alcoholic ferric chloride.

**$\beta$ -Methyl- $\gamma$ -nitrosotropolone** (I; R = NO, R' = H).— $\beta$ -Methyltropolone (0.5 g.) was dissolved in acetic acid (5 ml.), and water (10 ml.), containing hydrochloric acid (1 ml.), was added. The solution was treated dropwise with a solution of sodium nitrite (0.3 g.) in water (3 ml.) during 30 minutes. Dilution with water (10 ml.) and filtration gave  $\beta$ -methyl- $\gamma$ -nitrosotropolone (0.268 g.), which crystallised from alcohol in plates, m. p. 178° (decomp.) (Found: C, 58.5; H, 4.5.  $C_8H_7O_3N$  requires C, 58.2; H, 4.3%), giving a brown ferric test.

**Reduction of  $\beta$ -methyl- $\gamma$ -nitrosotropolone.** The above nitroso-compound (0.11 g.) was reduced in alcohol (30 ml.) in the presence of 5% palladium—charcoal catalyst (0.05 g.). Hydrogen (30 ml., 2 mols.) was absorbed and, on concentration of the solution, yellow prisms were deposited (0.06 g.). Crystallisation from alcohol gave  $\gamma$ -amino- $\beta$ -methyltropolone, m. p. 224° (decomp.), alone or mixed with an authentic sample. Preparation of the *benzylidene* derivative confirmed the identity.

**$\alpha'$ -Amino- $\beta$ -methyltropolone** (I; R = H, R' = NH<sub>2</sub>).— $\beta$ -Methyl- $\alpha'$ -nitrotropolone (0.22 g.) in dioxan-alcohol (30 ml.; 1 : 1) was shaken with 5% palladium—charcoal (0.1 g.) in an atmosphere of hydrogen under atmospheric conditions. Hydrogen (82 ml., 3 mols.) was absorbed during about an hour. Removal of the catalyst and evaporation of the solvent gave a crystalline residue which was sublimed at 120°/10 mm. Crystallisation from a little alcohol gave yellow prisms of  $\alpha'$ -amino- $\beta$ -methyltropolone (0.16 g.), m. p. 136—137° (Found: C, 63.1; H, 6.0; N, 9.5.  $C_8H_9O_3N$  requires C, 63.5; H, 6.0; N, 9.3%), which gave a deep green ferric test and dissolved in dilute alkali or acid to give yellow solutions.

**$\alpha$ -Amino- $\beta$ -methyltropolone** (IV; R = NH<sub>2</sub>).— $\beta$ -Methyl- $\alpha$ -nitrotropolone (0.18 g.) was reduced in the same manner as above. Sublimation of the residue at 130°/11 mm. gave  $\alpha$ -amino- $\beta$ -methyltropolone (0.12 g.), which crystallised from water as pale yellow prisms, m. p. 150—151° (Found: C, 63.1; H, 6.2; N, 9.2%), which gave a deep green ferric colour and dissolved readily in dilute acid and alkali.

**Diazotisation and Rearrangement of  $\alpha'$ -Amino- $\beta$ -methyltropolone.**— $\alpha'$ -Amino- $\beta$ -methyltropolone (0.04 g.) in N-sulphuric acid (3 ml.) was treated dropwise with sodium nitrite (0.03 g.) in water (0.5 ml.) at 0°. An orange solution immediately formed and treatment of a small portion with alkaline  $\beta$ -naphthol gave an intense red precipitate. The diazonium solution was gently warmed, whereupon decomposition occurred and a colourless suspension was produced. The precipitate (0.033 g.) was sublimed at 130°/11 mm. and crystallised from water to give colourless flat needles, m. p. 177° (Found: C, 63.1; H, 5.5. Calc. for  $C_8H_9O_3$ : C, 63.2; H, 5.3%), unchanged by admixture with a sample of 4-methyl-salicylic acid (V; R = Me, R' = H) prepared by alkali fusion of 4-methylsalicylaldehyde (Tiemann and Schotten, *loc. cit.*).

**Diazotisation and Rearrangement of  $\alpha$ -Amino- $\beta$ -methyltropolone.**—The  $\alpha$ -amino-tropolone (0.035 g.) was treated as above and reacted similarly. The precipitate (0.028 g.) was sublimed at 130°/11 mm., and the sublimate separated from water as needles, m. p. 170—171° (Found: C, 63.6; H, 5.7%. Calc.

[1951]

## New Syntheses of Cystine.

2071

for  $C_8H_8O_3$ : C, 63.2; H, 5.3%), found to be identical with 6-methylsalicylic acid (V; R = H, R' = Me) a sample of which was prepared from 2-methyl-6-nitrobenzonitrile by hydrolysis (Gabriel and Thieme, *loc. cit.*), reduction to the amino-acid by the usual catalytic method, and replacement of the amino-group by hydroxyl through the diazonium sulphate (Mayer and Schulze, *loc. cit.*).

*Ultra-violet Absorption Spectra.*—Ultra-violet absorption spectra were determined in methanolic solution, a Beckman Quartz Spectrophotometer being used. Ionisation of the nitro-tropolones was suppressed by addition of 0.1% of acetic acid to the methanolic solution. A summary of the results is given below. The figures given in italics represent points of inflection.

Substituent in $\beta$ -methyltropolone.	$\lambda_{\max.}$	$\log \epsilon_{\max.}$	$\lambda_{\max.}$	$\log \epsilon_{\max.}$	$\lambda_{\max.}$	$\log \epsilon_{\max.}$
$\gamma$ -NH <sub>2</sub> .....	2370	4.38	3600	4.12	3880	4.17
$\alpha$ -NH <sub>2</sub> .....	2570	4.56	3350	4.02	3980	3.93
$\alpha'$ -NH <sub>2</sub> .....	2560	4.51	3390	4.10	4060	3.90
$\gamma$ -NO <sub>2</sub> .....	2320	4.39	2370	4.34	3550	3.92
$\alpha$ -NO <sub>2</sub> .....	2400	4.46	3200	3.83	3620	3.76
$\alpha'$ -NO <sub>2</sub> .....	2450	4.42	3170	3.69	3750	3.78
$\gamma$ -I .....	2370	4.37	3360	4.04	3790	3.64
$\gamma$ -OH .....	2420	4.49	3350— 3700	constant at 3.99		
Substituent in salicylic acid.						
6-Me .....	2400	3.75	3070	3.52		
4-Me .....	2380	3.90	2970	3.64		

Our thanks are due to the University of Western Australia for a Hackett Research Studentship (to P. R. J.), and to Imperial Chemical Industries Limited for a grant which defrayed some of the expenses of this investigation.

THE UNIVERSITY, SHEFFIELD, 10.

[Received, April 28th, 1951.]