

NOTES.

The Chloro- and Iodo-acetates of Dihydrolanosterol and Dihydroagnosterol. By R. G. CURTIS.

THE X-ray examinations of derivatives containing atoms of high atomic weight have given considerable information concerning the arrangement of the rings and side chain in sterols (Crowfoot and Dunitz, *Nature*, 1948, **162**, 608). It is intended to apply this method of structure analysis to some of the wool-wax triterpenes, and for this purpose the iodoacetates of dihydrolanosterol and dihydroagnosterol have been prepared. They were obtained from the corresponding chloroacetates, potassium iodide, and acetone, the chloroacetates being readily prepared from chloroacetic anhydride and the alcohol. Attempts to esterify dihydrolanosterol and dihydroagnosterol with iodoacetyl chloride directly were not successful.

Experimental.—(a) *Dihydrolanosteryl chloroacetate* was prepared by heating dihydrolanosterol (5 g.) with chloroacetic anhydride (15 g.) on a steam-bath (3 hours); water was added, the mixture was warmed to destroy excess of anhydride, and the solid was washed with hot water and recrystallised three times

from hot chloroform (20 ml.)—methanol (60 ml.), to give fine white needles (3.6 g.), m. p. 114.5—115°, $[\alpha]_D^{20} +57.1^\circ$ (*c*, 3 in chloroform) (Found: C, 76.2; H, 10.5. $C_{32}H_{53}O_2Cl$ requires C, 76.1; H, 10.6%).

(b) *Dihydroagnosteryl chloroacetate* prepared in like manner from dihydroagnosterol (5 g.) formed prisms (3.4 g.), m. p. 143.5—144°, $[\alpha]_D^{24} +89.3^\circ$ (*c*, 3 in chloroform) (Found: C, 76.4; H, 10.0. $C_{32}H_{51}O_2Cl$ requires C, 76.4; H, 10.2%).

(c) *Dihydrolanosteryl iodoacetate* was prepared by refluxing (3 hours) the chloroacetate (1 g.) in acetone (50 ml.) with potassium iodide (3 g.). After removal of the solvent and thorough washing of the residue with water, three crystallisations from chloroform—methanol (1:3; 15 ml.) gave glistening prisms (0.65 g.), m. p. 105—105.5°, $[\alpha]_D^{21} +52.9^\circ$ (*c*, 3 in chloroform) (Found: C, 64.6; H, 8.7; I, 21.3. $C_{32}H_{53}O_2I$ requires C, 64.6; H, 8.95; I, 21.3%).

Dihydrolanosterol, m. p. 142—143°, was obtained by hydrolysis of the iodoacetate with alcoholic potassium hydroxide (4%).

(d) *Dihydroagnosteryl iodoacetate* prepared in like manner from dihydroagnosteryl chloroacetate (1 g.) and thrice crystallised formed glistening plates (0.85 g.), m. p. 114—114.5°, $[\alpha]_D^{23} +67.5^\circ$ (*c*, 3 in chloroform) (Found: C, 64.6; H, 8.6; I, 21.1. $C_{32}H_{51}O_2I$ requires C, 64.6; H, 8.6; I, 21.3%). Dihydroagnosterol, m. p. 154—155°, was obtained by hydrolysis of the iodoacetate with alcoholic potassium hydroxide (4%).

The dihydrolanosterol, m. p. 146—147°, $[\alpha]_D +62.8^\circ$ (*c*, 3 in chloroform), and dihydroagnosterol, m. p. 158—159°, $[\alpha]_D +67.5^\circ$ (*c*, 3 in chloroform), used were prepared according to the methods described by F. J. McGhie ("Contributions to the Chemistry of the Sterols," Thesis, London, 1947).

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The Nitration of *pp'*-Dichloroazobenzene. By C. D. HOUGHTON and WILLIAM A. WATERS.

PREVIOUS workers (cf. Burns, McCombie, and Scarborough, *J.*, 1928, 2928) have established that azobenzene and many of its derivatives nitrate and brominate in the *para*-position to the azo-group. Further, the nitrations of both the *o*- and the *m*-methylazobenzenes in the 4- and 4'-positions and the bromination of *m*-methylazobenzene in the 4-position indicate that the azo-group (or possibly the phenylazo taken as a whole) has a greater orienting power than the methyl group. In connection with another investigation (see Ford, Waters, and Young, *J.*, 1950, 833) it was of interest to determine, from the mode of cationoid substitution of *pp'*-dichloroazobenzene, the relative orienting powers of the chloro- and azo-groups, and consequently both the nitration and the bromination of *pp'*-dichloroazobenzene have been examined.

The nitration of *pp'*-dichloroazobenzene with fuming nitric acid in glacial acetic acid solution yields a dichloronitroazoxybenzene, m. p. 134°, which can also be obtained by the direct nitration of *pp'*-dichloroazobenzene. Under less drastic conditions nitration of the azo-compound does not occur. The product, m. p. 134°, has previously been obtained from *pp'*-dichloroazoxybenzene by both Calm and Heumann (*Ber.*, 1880, **13**, 1184) and Heumann (*Ber.*, 1872, **5**, 912), but these early investigators did not attempt to determine its exact structure. Calm and Heumann showed that their azoxy-compound could be reduced with cold alcoholic ammonium sulphide to a 4:4'-dichloro-nitroazobenzene. We have repeated this work, and have now found that this nitro-compound, on further reduction with tin and hydrochloric acid, yields a mixture of amines from which, by condensation with phenanthraquinone, we have been able to isolate 6-chloro-1:2:3:4-dibenzphenazine, identical with the product prepared by Ullmann and Mauthner (*Ber.*, 1904, **36**, 4028) from 4-chloro-*o*-phenylenediamine.

The nitration of *pp'*-dichloroazobenzene therefore yields 4:4'-dichloro-2-nitroazoxybenzene. Whether the nitration of the azo-compound precedes its oxidation, or the reverse, is as yet undecided, but it is now clear that both the azo- and the azoxy-group have a very marked *ortho-para* orienting power.

We failed to achieve the direct bromination of *pp'*-dichloroazobenzene, but prepared a sample of 4:4'-dichloro-2-bromoazobenzene for reference purposes.

Experimental.—*pp'*-Dichloroazobenzene was prepared by condensing *p*-chloronitrosobenzene with *p*-chloroaniline, whilst *pp'*-dichloroazoxybenzene was obtained as a by-product of the preparation of *p*-chloronitrosobenzene.

4:4'-Dichloro-2-nitroazoxybenzene was obtained by dissolving *pp'*-dichloroazobenzene (3 g.) in a mixture of fuming nitric acid (50 ml.) and glacial acetic acid (20 ml.) at -10° . The mixture was poured into water after keeping it at 0° for 30 minutes, and the solid was collected and crystallised repeatedly from alcohol. It formed fine yellow needles, m. p. 134° (Found: C, 46.6; H, 2.2; N, 13.4. $C_{12}H_7O_2N_3Cl_2$ requires C, 46.5; H, 2.2; N, 13.4%). The same product was obtained by dissolving *pp'*-dichloroazoxybenzene in a similar mixture of nitric and acetic acids.

4:4'-Dichloro-2-nitroazobenzene was prepared by keeping the nitro-azoxy-compound overnight with a mixture of equal volumes of ethyl alcohol and saturated ammonium sulphide solution. The product was precipitated with water, collected, and freed from sulphur by crystallisation from alcohol. It formed deep orange-red needles, m. p. 210° (Found: C, 48.9; H, 2.35; N, 14.2. $C_{12}H_7O_2N_3Cl_2$ requires C, 49.0; H, 2.4; N, 14.2%). An attempt to synthesise this compound by condensing together *p*-chloronitrosobenzene and 4-chloro-2-nitroaniline failed; the nitro-amine could be recovered unchanged after the two substances had been heated under reflux in glacial acetic acid.

4:4'-Dichloro-2-nitroazobenzene (5 g.) was reduced by boiling it with granulated tin (5 g.) in alcohol under reflux, and adding, from time to time, small portions (2—3 ml.) of concentrated hydrochloric acid until most of the tin had dissolved. The solution was then filtered from tin, diluted with one quarter of its volume of water, boiled for $\frac{1}{2}$ hour (charcoal), and refiltered. This filtrate was then heated for 10 minutes with an aqueous solution of phenanthraquinone (3.6 g.), sodium acetate (5 g.), and sodium

hydrogen sulphite (5 g.). 6-Chloro-1 : 2 : 3 : 4-dibenzphenazine gradually separated in filterable form. After crystallisation three times from nitrobenzene-glacial acetic acid (equal volumes) it formed pale yellow-green needles, m. p. 245°, which on sublimation in a vacuum gave white, feathery crystals, m. p. 246° (Found : C, 76.4; N, 8.8; Cl, 11.2. Calc. for $C_{20}H_{11}N_2Cl$: C, 76.4; N, 8.9; Cl, 11.3%). Ullmann and Mauthner (*loc. cit.*) describe this compound as forming pale yellow-green needles, m. p. 246°.

4 : 4'-Dichloro-2-bromoazobenzene was obtained by heating 4-chloro-2-bromoaniline (1.2 g.) with *p*-chloronitrosobenzene (0.8 g.) in glacial acetic acid at 100° for 10 minutes. The product crystallised from alcohol in orange-red needles, m. p. 145° (Found : C, 44.0; H, 2.1; N, 8.4. $C_{12}H_7N_2Cl_2Br$ requires C, 43.9; H, 2.2; N, 8.5%).

pp'-Dichloroazobenzene resisted bromination (i) by refluxing with bromine in glacial acetic acid solution in the presence of anhydrous sodium acetate, (ii) by heating for 10 hours at 100° with liquid bromine and a few drops of pyridine, and (iii) by heating at 100° in 90% sulphuric acid in the presence of both bromine and silver sulphate (compare Derbyshire and Waters, *J.*, 1950, 573).—THE DYSON FERRINS LABORATORY, OXFORD. [Received, December 15th, 1949.]

p-Cymene-2-sulphonamides. By (Miss) S. M. BROWN and G. H. THOMSON.

DURING the investigation of new surface-active agents, it was found that some amine derivatives of *p*-cymene-2-sulphonyl chloride are more difficult to prepare than the corresponding derivatives from benzene- and toluene-sulphonyl chlorides.

All b. p.s and m. p.s are uncorrected.

Preparation of Pure p-Cymene.—Commercial *p*-cymene (1 kg.) was shaken three times with concentrated sulphuric acid (900 c.c. in all); the top layer was washed successively with water, 1% potassium permanganate solution, 2*N*-potassium carbonate solution, and water again, dried (Na_2SO_4), and distilled; b. p. 175–176°; yield, 510 g.

p-Cymene-2-sulphonyl Chloride.—*p*-Cymene (67 g.) at 0° was added dropwise to stirred, ice-cold chlorosulphonic acid (180 c.c.) (B.D.H. techn.), the temperature being kept below 5°. When the addition was complete (90 minutes), the mixture was poured on 2 kg. of crushed ice, and the oily layer separated, washed, dried, and distilled; it had b. p. 163–165°/15 mm.; yield, 75 g. The sulphonamide, m. p. 115° (Found : N, 6.62. Calc. for $C_{10}H_{15}O_2NS$: N, 6.57%), was obtained quantitatively from the chloride, but the overall yield (84–87%) quoted by Huntress and Autenrieth (*J. Amer. Chem. Soc.*, 1941, 63, 3446) was not attained.

Substituted Amides.—The amine (2 g.) was shaken with 10% sodium hydroxide (20 c.c.), and *p*-cymene-sulphonyl chloride (6 g.) added in one-fifth portions; the mixture was shaken for 5 minutes after each addition. After 15 minutes' boiling and 2 hours' storage, a solid product was obtained, which formed white crystals from ethanol: *p*-Cymene-2-sulphonamide (2-methyl-5-isopropylbenzenesulphonamide) had m. p. 132.5° (Found : N, 4.90. $C_{16}H_{19}O_2NS$ requires N, 4.84%); the cyclohexylamide had m. p. 82° (Found : N, 4.74. $C_{18}H_{25}O_2NS$ requires N, 4.71%), and the *o*-, *m*-, and *p*-toluidine analogues had m. p. 101°, 101.5°, and 129°, respectively (Found : N, 4.7, 4.7, 4.7, respectively. $C_{17}H_{21}O_2NS$ requires N, 4.6%).

Derivatives from benzidine and 4-methyl-1 : 3-phenylenediamine. Benzidine (2.3 g.) or 3-methyl-1 : 4-phenylenediamine (1.5 g.) was shaken with 10% sodium hydroxide (40 c.c.), and the sulphonyl chloride (6 g.) added in one-fifth portions, the mixture being boiled after each addition and finally boiled under reflux for 1 hour and then set aside overnight. The benzidine analogue of the above formed grey crystals from *n*-butanol, m. p. 257–258° (Found : N, 7.35. $C_{22}H_{24}O_2N_2S$ requires N, 7.37%), and the 4-methyl-1 : 3-phenylenediamine derivative formed grey crystals from ethanol (Found : N, 9.10. $C_{17}H_{22}O_2N_2S$ requires N, 8.81%), m. p. 166°. In neither case did further treatment with the sulphonyl chloride raise the m. p.

Morpholine derivative. Morpholine (4.4 g.) was added to a solution of *p*-cymenesulphonyl chloride (6 g.) in benzene (15 c.c.). The morpholine hydrochloride which was immediately precipitated was filtered off, and the benzene removed in a vacuum at 30°. The resultant glass was triturated with light petroleum (b. p. 60–80°) and then recrystallised once from ethanol and twice from light petroleum. The morpholide formed white crystals, m. p. 62.5° (Found : N, 5.06. $C_{14}H_{21}O_3NS$ requires N, 4.95%).

Piperidine derivative. Piperidine (2 g.) was shaken with 10% sodium hydroxide (20 c.c.), and *p*-cymenesulphonyl chloride (9 g.) added in one-fifth portions. After being boiled for 30 minutes and kept overnight, the oily product was extracted with ether, and the extract washed and dried (Na_2SO_4). The ether was removed, and the oil distilled in a vacuum. The piperidide, b. p. 222–225°/15 mm., was colourless, but could not be induced to crystallise (Found : N, 5.00. $C_{15}H_{23}O_2NS$ requires N, 4.98%).

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Fluorescence and the Beer-Lambert Law. A Note on the Technique of Absorption Spectrophotometry.

By E. A. BRAUDE, J. S. FAWCETT, and C. J. TIMMONS.

ONE of the fundamental principles of quantitative absorption spectrophotometry is the assumption that the intensity of absorption is directly proportional to, and that the extinction coefficient is independent of, the concentration of absorbent (Beer's law) and the length of the absorption path (Lambert's law). As far as we are aware, the validity of Lambert's law has never been questioned. Deviations from Beer's law, on the other hand, are quite frequently encountered, but it appears generally accepted that this is always due to concentration-dependent chemical equilibria such as association or ionisation

reactions. In general, however, simple organic compounds in neutral solution are assumed to obey the Beer-Lambert law, and in many cases the validity of the law has been tested and explicitly confirmed.

We have repeatedly observed (cf. Braude, Fawcett, and Newman, *J.*, 1950, 793) in the course of work with a wide variety of organic compounds, that the ultra-violet light absorption of substances which exhibit strong fluorescence in solution appears to vary markedly with both concentration and cell length. Moreover, smaller but nevertheless significant deviations from the Beer-Lambert law are found with many compounds which do not exhibit visible fluorescence, and the magnitude of the effects is closely dependent on the type of instrument and the experimental conditions employed. Although none of the compounds concerned would be expected to undergo any reversible reactions in dilute neutral solutions, such an explanation can never be rigidly ruled out for the deviations from Beer's law; the deviations from Lambert's law, on the other hand, which are equally or even more pronounced in these cases, can only be physical in origin. As will be shown in the sequel, it is very probable that the variations of extinction coefficient with concentration are due to the same cause as the variations with cell length, namely to the superposition of transmitted light and scattered fluorescence emission. This phenomenon appears to have escaped notice hitherto and the purpose of this note is to draw attention to the important bearing which it has on the widely employed techniques of absorption spectrophotometry.

Although relatively few quantitative measurements of the fluorescence spectra of organic compounds in solution have been recorded (cf. Hausser, Kuhn, and Kuhn, *Z. physikal. Chem.*, 1935, B, 29, 417; Kortüm and Finckh, *ibid.*, 1942, B, 52, 263; Ley and Specker, *Z. wiss. Photographie*, 1939, 38, 13; Schoental and Scott, *J.*, 1949, 1683), it is known that unsaturated compounds which exhibit selective ultra-violet or visible-light absorption also give rise to fluorescence emission in the same region. Generally, the fluorescence spectrum is at longer wave-lengths than the absorption spectrum, but in polyatomic compounds some overlap often occurs owing to the close spacing of vibrational levels (cf. Bowen, *Quarterly Reviews*, 1947, 1, 1). It is clear that if, in absorption measurements, any of the fluorescence emission reaches the recording device, the apparent intensity of transmitted light at that wave-length will be increased, *i.e.* the apparent intensity of absorption reduced, and that the magnitude of this effect will depend on the ratio of the intensities of the recorded fluorescence emission and of the transmitted light. It is necessary to distinguish between two types of instrument, (*a*) those in which the light is dispersed *after* passing through the absorbent (*e.g.* the Hilger Spekker spectrophotometer and most other photographic instruments) and (*b*) those in which the light is dispersed *before* passing through the absorbent (*e.g.* the Beckman and other photoelectric spectrophotometers). In type (*a*) a fraction of the fluorescence emission will be scattered into the slit of the spectrometer and will reach the recording device after dispersion, giving rise to an apparent decrease in absorption intensity at the wave-length of the *fluorescent* light. In this arrangement, the effect will be relatively small (*i.e.* only noticeable with strongly fluorescent substances or bands) and will be spread over the spectrum. It will be larger at high extinctions, when the intensity of real transmitted light is small, but the precise relationship between the extinction coefficient and the concentration and the cell-length may be influenced by at least the following additional factors: (i) decrease of fluorescence intensity at increasing concentrations owing to quenching effects, (ii) change in scattering properties with cell-length and cell shape, and (iii) increasing re-absorption of scattered fluorescence emissions with increasing cell-length. In instruments of type (*b*), the fluorescence emission will be scattered directly into the photoelectric cell, giving rise to an apparent decrease in absorption intensity at the wavelength of the *absorbed* light, and owing to the greater proximity of the cell to the recording device, the effect of the fluorescence emission will be much larger in this type of instrument than in type (*a*). As before, deviations from the Beer-Lambert law will be largest at high extinctions when the intensity of the transmitted light is small. The effect will therefore generally increase with increasing concentration at constant cell-length, and with increasing cell-length at constant concentration, subject to the additional factors mentioned above.

The fluorescence effect is illustrated below by measurements of the highest-intensity bands of naphthalene, anthracene, and styryldimethylcarbinol, using a Beckman photoelectric spectrophotometer (Model DU). Whereas potassium chromate gives concordant intensity values over the whole range of extinctions ($E = 0.1-2.5$) and cell lengths (0.1-1.0 cm.) employed, the apparent extinction coefficients for the organic compounds show startling variations, ϵ decreasing strongly at high extinctions. The deviations from the Beer-Lambert law generally become appreciable for extinctions above 1.0, and for extinctions higher than 2.0, ϵ actually decreases with increasing concentration in the case of naphthalene and anthracene. Under these conditions, the intensity of the fluorescent light is evidently greater than that of the transmitted light and therefore the fluorescent intensities in these examples are of the order of one hundredth of the intensity of the incident light. As would be expected, extinction readings in the region where the fluorescence effect is appreciable vary somewhat with the slit width employed. Deviations of a smaller order are also exhibited by the longer-wave-length, lower-intensity bands of naphthalene and anthracene. Using a Hilger Spekker photographic spectrophotometer, on the other hand, the Beer-Lambert law is obeyed almost within experimental error ($\pm 2\%$) in agreement with the findings of Mayneord and Roe (*Proc. Roy. Soc.*, 1935, A, 152, 299) and the extinction coefficients correspond fairly closely to the highest values of ϵ obtained with the photoelectric instrument.

The results obtained with styryldimethylcarbinol show that the fluorescence effect is by no means limited to polycyclic aromatic derivatives (cf. Braude, Fawcett, and Newman, *J.*, 1950, 793). Since all compounds exhibiting selective absorption in the ultra-violet may theoretically also exhibit fluorescence, deviations from the Beer-Lambert law would indeed be expected to be quite general, but the magnitude of the effect will obviously depend on the wave-lengths and the intensities of the fluorescence bands and little is known at present concerning the dependence of fluorescence on structure in simple unsaturated systems. Using a Beckman instrument, we have observed appreciable deviations from the Beer-Lambert law with other styryl derivatives, but not with benzoic acid or conjugated acyclic dienes.

These findings are of obvious significance in relation to the use of light-absorption data for the characterisation and analysis of organic compounds and in relation to the choice and design of instruments. It is evidently desirable that the Beer-Lambert law should be tested wherever possible

and that the conditions of measurement should be more closely defined than has been the practice hitherto. The extinction range $E = 0.3-0.7$ is usually regarded as instrumentally the most accurate in photoelectric photometry, and the possibility of fluorescence emission provides additional reason for avoiding higher extinctions.

Beckman Photoelectric Spectrophotometer.

c = Concentration in g.-mols./l. l = Cell length in cm. E = Extinction (optical density) reading. ϵ = Apparent molecular extinction coefficient = E/cl

(i) Potassium chromate in 0.05M-aqueous potassium hydroxide. Maximum at 2725 Å.

10^4c	0.285	0.700	2.08	4.87	5.58	3.48				
l	1.0					0.1	0.2	0.33	0.5	1.0
E	0.104	0.251	0.748	1.75	2.38	0.123	0.248	0.423	0.625	1.23
ϵ	3,660	3,580	3,580	3,540	3,620	3,540	3,560	3,640	3,580	3,620

(ii) Naphthalene in ethanol. Maximum at 2200 Å.

10^4c	0.012	0.065	0.15	0.25	0.35	1.55	0.47			
l	1.0					0.1	0.2	0.33	0.5	1.0
E	0.119	0.618	1.39	2.05	2.35	2.32	0.518	1.16	1.69	2.28
ϵ	99,000	95,000	93,000	82,000	67,000	15,000	110,000	108,000	108,000	97,000

(iii) Anthracene in ethanol. Maximum at 2510 Å.

10^4c	0.011	0.033	0.055	0.099	0.132	0.154	0.275	0.860	1.38	4.50
l	1.0					0.1	0.2	0.33	0.5	1.0
E	0.188	0.565	0.930	1.537	1.865	1.965	2.15	2.22	2.23	2.21
ϵ	170,000	171,000	170,000	156,000	142,000	128,000	78,500	27,000	16,000	4,900

10^4c	2.75				
l	0.1	0.2	0.33	0.5	1.0
E	0.473	0.933	1.558	1.860	2.05
ϵ	172,000	170,000	170,000	136,000	74,500

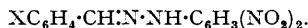
(iv) Styryldimethylcarbinol in 60% aqueous dioxan. Maximum at 2510 Å.

10^4c	0.11	0.29	0.55	1.10	4.27	2.14				
l	1.0					0.1	0.2	0.33	0.5	1.0
E	0.212	0.535	0.946	1.53	1.75	0.394	0.738	1.20	1.685	1.74
ϵ	19,300	18,500	17,200	13,900	4,100	18,400	17,200	16,800	14,800	8,100

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The Dinitrophenylhydrazones of the Halogenobenzaldehydes. By O. L. BRADY and S. G. JARRETT.

WHILE the various halogenobenzaldehydes were available in connection with other work their 2 : 4-dinitrophenylhydrazones have been prepared by addition of the aldehyde (2 g.), dissolved in a small quantity of alcohol, to a hot solution of 2 : 4-dinitrophenylhydrazine sulphate [prepared by the addition of concentrated sulphuric acid (4 c.c.) to a suspension of 2 : 4-dinitrophenylhydrazine (2 g.) in alcohol (50 c.c.)] whereupon the dinitrophenylhydrazones separated. They crystallised from xylene in orange crystals except where otherwise stated. In place of the aldehydes the oximes can be used; as these can be purified by crystallisation, purer products can be obtained from them than from the liquid aldehydes.



X.	M. p.	Found, %.		X.	M. p.	Found, %.		X.	M. p.	Found, %.	
		C.	H.			C.	H.			C.	H.
<i>o</i> -F	200°	51.8	3.0	<i>o</i> -Br	203°	43.2	2.6	<i>o</i> -I	215°	38.5	2.2
<i>m</i> -F	266	51.5	2.8	<i>m</i> -Br	257	43.1	2.5	<i>m</i> -I	258	38.2	2.3
<i>p</i> -F	278	51.2	3.0	<i>p</i> -Br	257	42.9	2.8	<i>p</i> -I*	258	38.3	2.2

($\text{C}_{13}\text{H}_9\text{O}_4\text{N}_4\text{F}$ requires
C, 51.3; H, 3.0%.)

($\text{C}_{13}\text{H}_9\text{O}_4\text{N}_4\text{Br}$ requires
C, 42.7; H, 2.5%.)

($\text{C}_{13}\text{H}_9\text{O}_4\text{N}_4\text{I}$ requires
C, 37.9; H, 2.2%.)

* Scarlet crystals.

The dinitrophenylhydrazones of the chlorobenzaldehydes have been described by Blanksma and Wacker (*Rec. Trav. chim.*, 1936, **55**, 658), Ferranti and Bloom (*Amer. J. Pharm.*, 1933, **105**, 381), Eitel and Lock (*Monatsh.*, 1939, **72**, 289), and Graymore and Davies (*J.*, 1945, 293). The melting points of our specimens were: *o*-compound 210° and *m*-compound 255°, which are within 1° of the values given by Blanksma and Wacker but considerably different from those of some other workers. For the *p*-chloro-compound (Found: C, 49.1; H, 2.8. Calc. for $\text{C}_{13}\text{H}_9\text{O}_4\text{N}_4\text{Cl}$: C, 48.7; H, 2.8%) we find m. p. 266° as compared with 216°, 224°, and 218—220° given by other workers. It seems probable that our compound was an isomeric form like others previously noticed among dinitrophenylhydrazones. It may be noted that the melting points given by other workers for the *p*-compound are between those for the *o*- and *m*-derivatives, which is contrary to general experience with compounds of this type.—THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON. [Received, January 17th, 1950.]