STUDIES IN LIGHT ABSORPTION AND THE REACTIONS BETWEEN SUBSTITUTED PHENYLHYDRAZINES AND AROMATIC ALCOHOLS

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STUDIES IN
LIGHT ABSORPTION
AND
THE REACTIONS BETWEEN
SUBSTITUTED PHENYLHYDRAZINES
AND
AROMATIC ALCOHOLS

A THESIS
BY
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Submitted to the Committee of graduate studies of the Memorial University of Newfoundland in partial fulfillment of the requirements for the degree of M.Sc.
I wish to express my gratitude to my supervisor, Dr. W.F. Forbes for the advice and encouragement I have received from him while this work was being performed. I also wish to acknowledge the receipt of a grant from the National Research Council of Canada.
ABSTRACT

In part I the absorption spectra of a number of substituted benzoic acids and phenyl benzoates are discussed from the point of view of the electrical and steric effect of the substituent. The spectral changes in the B band are correlated with these effects and the orders of magnitude of the inductive and mesomeric effects have been found to be similar to the orders found by chemical measurements. The conjugation of the non-bonded p-electrons of the oxygen-atom in phenyl benzoate with the \( \pi \)-electrons of the phenyl-group has been investigated.

Part II consists of a critical survey of past and present theories concerning the oxidation of sugars and unsaturated alcohols by phenylhydrazine and its derivatives. Some experimental work is described and it is concluded that none of the present theories satisfactorily account for all of the known facts.
The absorption band observed in the 230mμ region of the absorption spectrum, and designated by Moser and Kohlenberg as the B band, is of interest in ortho-substituted benzoic acids, since the observed spectra cannot be accounted for entirely by consideration of the steric effect of an ortho-substituent. Since it has been shown in studies of the spectra of acetophenones that one should compare the spectrum of the ortho-substituted compound with that of the para-substituted compound rather than with that of the unsubstituted aldehyde or ketone, this scheme will be adopted in the following discussion of substituted benzoic acids.

The formula of benzoic acid may be written in two ways: viz. type IA or type IB (R = H)

![Formula](image)

Benzoic acid itself may be considered to be made up of

molecules in various energy levels between these two extreme forms. However, if only steric phenomena are considered, neither of these forms satisfactorily explains the observed spectra of ortho-substituted benzoic acids. For if it is considered that molecules of type A predominate, then the introduction of an ortho-methyl group would, from a comparison with o- and p-methyl acetophenones, be expected to produce a hypsochromic shift of approximately $10\text{m}\mu$, and a decrease in maximal absorption such that the ratio of molar extinction coefficients were approximately 0.57. In fact, the expected hypsochromic shift does take place, but the decrease in absorption intensity is such that the ratio is 0.36. This means that either there is more steric overlap in o-toluic acid than in o-methyl acetophenone between the same methyl-group and ostensibly the same carbonyl-group, or else structure 1A ($R = H$) does not truly represent benzoic acid.

Furthermore, by a consideration of o-toluic acid and 2,6-dimethylbenzoic acid, it can be shown that structure 1B ($R = H$) does not adequately represent benzoic acid; for if the introduction of one ortho-methyl-group produced a twist in the carbon-carbon bond sufficient to accommodate the substituent, then the introduction of a second ortho-methyl-group would be expected to make little further difference to the spectrum, whereas in 2,6-dimethylbenzoic acid the B band has disappeared completely\(^1\). Hence, if the effect of ortho-methyl-groups is entirely steric, neither
structure 1A nor structure 1B adequately explains the observed spectra. However, as these structures are the only logically possible extreme forms of benzoic acid, it may be concluded that the observed changes in the B band of substituted benzoic acids are the result of electrical effects which do not make themselves apparent in the spectra of acetophenones, in addition to the usual steric effects. These electrical effects take the form of an increased sensitivity to the steric influence of ortho-substituents. This increased sensitivity is ascribed to the increase in electron density in the carboxyl-group in the excited state of benzoic acid as compared with the electron density in the \( \text{CO}_2 \)-group in the excited state of acetophenone, and/or less double bond character in the carbon-carbon linkage. This greater electron density is due to the strong negative inductive effect of the hydroxyl-group of benzoic acid, contrasted with the small positive inductive effect of the methyl-group of acetophenone. Thus the hindrance postulated occurs chiefly in the excited state, which, as has been pointed out, explains the observation that the steric effect consists chiefly of decreased intensity of maximal absorption rather than a pronounced hypsochromic shift of the band. However, the ground state of benzoic acid is more stabilised by resonance forms than that of acetophenone, as the replacement of the methyl-group of acetophenone, or the hydrogen-atom of benzaldehyde by the hydroxyl-group
of benzoic acid assists in the up of polar excited states; thus the energy level of the ground state of benzoic acid is reduced relative to that of acetophenone, and this, together with the relative increase in energy of the excited state gives rise to considerably greater energy difference in the case of benzoic acid. Thus, benzoic acid, and substituted benzoic acids, absorb maximally at a much shorter wave-length and lower intensity than the corresponding substituted acetophenones and benzaldehydes. (c.f. Benzoic acid, $A_{\text{max.}}$, 227m, $E = 11,000$. Acetophenone, $A_{\text{max.}}$, 240m, $E = 12,500$. Benzaldehyde, $A_{\text{max.}}$, 244m, $E = 13,000$).

Electrical effects may be divided into inductive effects, directly dependent on the electronegativities of the atoms concerned, and mesomeric (or resonance) effects, i.e. the capacity for sharing a pair of electrons with a neighbouring atom. The inductive effect follows approximately the inverse square law, and so is not generally transmitted past more than one or two atoms. Therefore, this effect will assume greater importance in the ortho-position than in the meta- or para- positions. The mesomeric effect is generally considered to be of equal importance in ortho- and para-positions. Of the substituents discussed here, methyl-groups exert a positive inductive effect, i.e. they repel electrons, while nitromethoxy- and hydroxyl-groups and the halogens exert a negative inductive effect, the order of the halogens being $F > Cl > Br > I$. Only the nitro-group exerts a negative mesomeric effect, i.e. resonance structures of
type II tend to be set up, while all the others exert a positive mesomeric effect, i.e. resonance structures of type III tend to be set up,

$$\text{II} \quad \text{III}$$

the order of the halogens being $\text{I} > \text{Br} > \text{Cl} > \text{F}$.

**para-Substituted Benzoic Acids**

Table I shows that compared with benzoic acid, all para-substituted benzoic acids exhibit pronounced bathochromic shifts accompanied by enhanced intensity of absorption, both of which are approximately parallel with the mesomeric effect of the substituent, for example $\text{I} > \text{Br} > \text{Cl} > \text{F}$. As has been pointed out, the inductive effect is of relatively little importance in para-substituted compounds, and this is borne out by the observed correlation between the bathochromic shifts and intensity changes on the one hand, and the mesomeric effects of the substituents on the other. In this connection the reported values$^1$ for $p$-bromobenzoic acid ($\lambda_{\text{max.}}$, 240m$\mu$, $E = 12,500$) appeared to be slightly inaccurate, and a careful redetermination gave a value of $E = 16,000$ at 238.5m$\mu$, the wave-length of maximal absorption.
This value of $E = 16,00$ lies, as expected, between the values for the intensities at wave-length of maximal absorption of $p$-chlorobenzoic acid ($E_{\text{max.}} = 15,000$) and $p$-iodobenzoic acid ($E_{\text{max.}} = 17,000$) (See table I).

The spectrum of $p$-nitrobenzoic acid resembles that of nitrobenzene (See below) with a small increase in transition probability. This increase is due to the negative inductive effect of the carboxyl-group, which increases the probability of transitions of type II, meta-

Substituted Benzoic Acids

For meta-substituted benzoic acids, according to the above hypothesis, the inductive effect increases in importance, while at the same time the mesomeric effect is greatly reduced for groups for which this effect is positive, since the mesomeric electron release for these groups is transmitted more effectively to the ortho- and para- positions. Thus the spectra will resemble that of the unsubstituted acid, but with slightly decreased absorption intensity due to the adverse inductive effect. Appreciable changes in the wave-length of maximal absorption are observed only for meta-iodo- and meta-nitrobenzoic acids, and this may be ascribed to the characteristic behaviour of iodine-atoms and nitro-groups. In the iodobenzoic acids, the interaction of the iodine-atom and the carboxyl-group is readily apparent. The meta-compound, as compared with the para-compound exhibits appreciable loss of intensity of absorption, together with a pronounced change in location
together with a pronounced change in location of maximal absorption. This is of interest, since 2-iododiphenyl also exhibits a similar band in that region, unusual for a compound containing an iodophenyl group, which becomes apparent under conditions of slight steric strain.3.

**TABLE 1**

**ABSORPTION SPECTRA OF SUBSTITUTED BENZOIC ACIDS IN ABSOLUTE ETHANOL**

Wave-lengths and intensities of the "B" band maxima (Values underlined represent inflections)

<table>
<thead>
<tr>
<th>Acid</th>
<th>Position of Substituent</th>
<th>Ortho</th>
<th>Meta</th>
<th>Para</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(\lambda_{\text{Max.}})</td>
<td>(\epsilon_{\text{Max.}})</td>
<td>(\lambda_{\text{Max.}})</td>
</tr>
<tr>
<td>Benzoic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluic</td>
<td></td>
<td>228</td>
<td>5000</td>
<td>232</td>
</tr>
<tr>
<td>Fluorobenzoic</td>
<td></td>
<td>223</td>
<td>9500</td>
<td>225</td>
</tr>
<tr>
<td>Chlorobenzoic</td>
<td></td>
<td>229</td>
<td>6000</td>
<td>230</td>
</tr>
<tr>
<td>Bromobenzoic</td>
<td></td>
<td>234</td>
<td>6500</td>
<td>225</td>
</tr>
<tr>
<td>Iodobenzoic</td>
<td></td>
<td>233</td>
<td>7000</td>
<td>284</td>
</tr>
<tr>
<td>Hydroxybenzoic</td>
<td></td>
<td>236</td>
<td>7500</td>
<td>236</td>
</tr>
<tr>
<td>Anisic</td>
<td></td>
<td>230</td>
<td>6000</td>
<td>230</td>
</tr>
<tr>
<td>Nitrobenzoic</td>
<td></td>
<td>255</td>
<td>3500</td>
<td>255</td>
</tr>
</tbody>
</table>

1. Values in 95% ethanol due to Moser and Kohlenberg.1
2. See experimental

In the nitrobenzoic acids the carboxyl-group, from an electrical point of view, appears to be of little consequence. The spectrum of \(p\)-nitrobenzoic acid is altered as might have been expected from steric considerations (i.e., steric interference of the nitro-group by the carboxyl-group), namely, the meta-compound exhibits a hypsochromic shift.

accompanied by loss of absorption intensity, and neither spectrum is radically different from that of nitrobenzene, which was found to absorb maximally at 258 μm, ε = 8,500.

A similar explanation, that is in terms of steric factors, holds for the spectra of toluic acids, in which the inductive effect is small. This steric effect becomes readily apparent in increasing order para < meta < ortho. The intermediate steric effect of the methyl-group in the meta-position may be accounted for by the known buttressing effect of a methyl-group in that position; that is, the methyl-group exerting a buttressing effect on the ortho-hydrogen atom which in turn sterically interacts with the carboxyl-group.

**ortho-Substituted Benzoic Acids**

From evidence involving Van der Waals' radii, Moser and Kohlenberg point out that shifts in the wave-lengths of the B band should not be assigned only to steric interference with coplanarity, but undoubtedly the best rationalisation of the recorded spectral values for ortho-substituted benzoic acids is obtained by a consideration of the steric factors involved. Also, Van der Waals' radii, are rather unsatisfactory as a measure of the intramolecular interference properties of atoms, particularly for groups containing hetero-atoms, whose electronegativity largely differs from that of the carbon-atom. Hetero-atoms may give rise to

appreciable mesomeric and inductive effects, the latter especially affecting any semi-quantitative interpretation of values.

Toluic acids have already been discussed. It is supposed that benzoic, ortho-toluic, and possibly 2,6-dimethylbenzoic acids are planar or near planar in the ground state, but the permitted number of excited states sharply decreases in the order benzoic acid \textsuperscript{)} ortho-toluic acid \textsuperscript{)} 2,6-dimethylbenzoic acid.

All the other above-mentioned ortho-substituted benzoic acids also show the expected hypsochromic shift of the absorption maxima accompanied by loss of absorption intensity compared with the corresponding para-compound. Substituents with large negative inductive effects, by stabilishing polar excited states of type IV increase the probability of transition. As expected, this is particularly obvious in compounds like o-fluorobenzoic acid, where in addition, the steric effect due to the fluorine-atom is small. There the ratio of the intensities at maximal absorption between the ortho- and the
para-compound is 0.86, which is much larger than for other pairs of ortho- and para-compounds (See table I). In toluic acid the positive inductive effect of the substituent increases the electron density in the carboxyl-group and the steric interaction between the ortho-methyl group and the carboxyl-group is greater than the interaction between the carboxyl-group and the larger ortho-methoxyl group, which have a negative inductive effect and thus reduce the electron density in the carboxyl-group. This explains the less pronounced loss in absorption intensities of salicylic and ortho-anisic acids compared with ortho-toluic acid (See table I). Furthermore, these data confirm the assumption that the inductive effect is of greater importance in the ortho-acids than in the para-acids, and exerts more influence on the spectra of ortho-acids than does the mesomeric effect.

Acetanilides

Applying this hypothesis to the recently investigated absorption spectra of substituted acetanilides⁵ (See table II), it is seen that the data correspond with the generalisations made. Thus, acetanilide itself, to which the steric considerations referred to under benzoic acid do not apply, absorbs maximally in a similar manner to acetophenone, due to transitions involving polar excited states of type V.

In para-substituted acetanilides, the intensity changes and shifts in location of maximal absorption again generally correspond to the mesomeric effect of the substituent. For example, 1 Br Cl F. The para-nitro group gives rise to a pronounced hypsochromic shift, which may be ascribed to the strong negative mesomeric effect of the substituent. This shift in location of maximal absorption, together with the accompanying decrease in absorption intensity indicates that there is definite interaction between the nitro-group and the NH.CO.CH₃-group. (Compare table I for the spectrum of p-nitrobenzoic acid where there appears to be no interaction).

For meta-substituted acetanilides, due to the ortho-para-directing properties of the NH.CO.CH₃-group, the spectra will even more resemble that of the unsubstituted acetanilide than was the case for meta-substituted benzoic acids. An exception is provided by m-nitroacetanilide where the combination of a negative inductive effect together with the negative mesomeric effect of the nitro-group stabilises excited states of type V, giving rise to considerably greater intensity of absorption.
Steric effects also become noticeable in some of these compounds, particularly where the substituent is large, such as in m-bromo- or m-iodoacetanilide (See table II). The nitroacetanilides as described above are of special interest. The negative mesomeric effect of the nitro-group decreases the electron density of all ring carbon-atoms, but the ortho- and para- positions are deactivated far more than the meta-position, which by comparison is almost unaffected. Thus, m-nitroacetanilide exhibits the largest absorption intensity. It is tentatively proposed that in o-nitroacetanilide the steric hindrance by the ortho-substituent inhibits the deactivation mechanism, and thus the spectrum of the ortho-compound reverts to a spectrum where the opposing mesomeric effect of the nitro-group is less noticeable (See table II).

In the other ortho-substituted acetanilides, the inductive effect plays its expected part. Substituents with a large negative inductive effect once again increase the transition probability. For example, the ratio of maximal absorption for the methyl-substituted acetanilides is 0.43, while for the methoxyl-substituted compounds it is 0.72; i.e. the same type of effect which was observed for the corresponding benzoic acids, for which the ratios are 0.36, and 0.43. This type of effect in the spectra of ortho-substituted acetanilides is, in general, strikingly similar to the effect observed in the benzoic acids, as a comparison of tables I and II will show, and this lends additional support to the proposed polar excited states of type V. Discussing ortho-substituted
acetanilides, Ungnade\textsuperscript{5} states that there are no steric effects in ortho-methoxyacetanilide, but a steric effect hypothesis accounts more satisfactorily for the observed spectrum. Ungnade argues that though the primary band of o-methoxy-acetanilide is somewhat less intense that that of the meta-isomer, the order of intensities is reversed for the secondary bands, and the wave-lengths of corresponding bands in the ortho- and meta-isomers are virtually identical. Here, it is suggested that the ortho-compound shows a typical steric effect of a type which has been discussed fully elsewhere\textsuperscript{2,4,6} in which the location of maximal absorption remains approximately the same, while the intensity of absorption is reduced. This effect becomes readily apparent if the ortho-compound is compared with the corresponding para compound, rather than with the meta-compound. This seems justified, since it has been shown in the study of acetophenones\textsuperscript{2,4} that the former comparison has the greater validity. A similar steric effect is proposed to explain the anisidine spectra referred to by Ungnade\textsuperscript{5}. Furthermore, since it has been shown in a number of other examples\textsuperscript{1,2} that the secondary band is not appreciably affected by steric interference of resonance, one would not expect the secondary band of acetanilides to exhibit a steric effect.

<table>
<thead>
<tr>
<th>Acetanilide</th>
<th>Position of Substituent</th>
<th>Ortho</th>
<th>Meta</th>
<th>Para</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \lambda_{\text{max}} ) ( \varepsilon_{\text{max}} )</td>
<td>( \lambda_{\text{max}} ) ( \varepsilon_{\text{max}} )</td>
<td>( \lambda_{\text{max}} ) ( \varepsilon_{\text{max}} )</td>
<td></td>
</tr>
<tr>
<td>Acetanilide</td>
<td>m( \mu )</td>
<td>m( \mu )</td>
<td>m( \mu )</td>
<td>m( \mu )</td>
</tr>
<tr>
<td>Methyl</td>
<td>230 6500 (242 14,500)</td>
<td>245 14,000</td>
<td>245 15,000</td>
<td>15,000</td>
</tr>
<tr>
<td>Fluoro</td>
<td>239 12500 242 15,100</td>
<td>240 13,000</td>
<td>13,000</td>
<td></td>
</tr>
<tr>
<td>Chloro</td>
<td>240 10500 245 14,900</td>
<td>249 18,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bromo</td>
<td>234 7500 246 14,000</td>
<td>252 18,500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iodo</td>
<td>shoulder 246 13,500</td>
<td>254 23,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methoxy</td>
<td>244 10500 245 11,500</td>
<td>249 15,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitro</td>
<td>233 17000 242 22,500</td>
<td>222 13,000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Aromatic Esters**

In the light of these hypotheses, an examination of the spectra reported by Cilento and the extension of this work to a number of other esters appeared to be of interest. The spectrum of phenyl benzoate is explained as follows: The spectra of benzoic acid and acetophenone have been correlated by contrasting the negative inductive effect of the hydroxyl-group of benzoic acid with the small positive inductive effect of the methyl-group of acetophenone. The steric factors postulated to be operative chiefly in the excited state of benzoic acid, and considered to be caused by the high electron density in the carboxyl-group are a little reduced in phenyl benzoate, since the phenyl-group attached to the oxygen-atom (henceforth referred to as ring B in accordance with Cilento's nomenclature) is an electron attracting group. It therefore removes some of the electrons.
responsible for the steric effect, and hence transitions to excited states of type VI are aided, accounting for the slight bathochromic and hyperchromic shifts.

![Diagram VI]

VI

The value for the observed intensity however, also includes some absorption due to ring B, i.e. due to transitions involving excited states of type VII.

![Diagram VII]

VII

In agreement with Cilento, bands are ascribed to transitions involving either ring A or ring B, although both bands will be influenced by the neighbouring ring.

From tables I and III, it is seen that substituents in ring A produce such spectral changes as would be expected from a consideration of the spectra of the corresponding benzoic acids. Since the para-substituent, on account of its mesomeric effect, will influence the electron cloud in the carboxyl-group, the change brought about by the introduction of the unsubstituted B ring will not necessarily be the same for each ester. Nevertheless, in most cases the difference
### TABLE III

**ABSORPTION SPECTRA OF AROMATIC ESTERS AND REFERENCE COMPOUNDS IN ABSOLUTE ETHANOL**

Wave-lengths and intensities of the main maxima (Values underlined represent inflections)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Substituent in Ring A</th>
<th>Ring A Band</th>
<th>Substituent in Ring B</th>
<th>Ring B Band</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ&lt;sub&gt;max.&lt;/sub&gt; Å</td>
<td>ε&lt;sub&gt;max.&lt;/sub&gt;</td>
<td>λ&lt;sub&gt;max.&lt;/sub&gt; Å</td>
<td>ε&lt;sub&gt;max.&lt;/sub&gt;</td>
</tr>
<tr>
<td>(Benzoic acid)</td>
<td>(227 11,000)</td>
<td></td>
<td>274 2,000</td>
<td></td>
</tr>
<tr>
<td>Phenyl benzoate</td>
<td>230 15,000</td>
<td>259 21,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenyl p-chlorobenzoate</td>
<td>p-Chloro</td>
<td>262 20,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenyl p-Iodobenzoate</td>
<td>p-Iodo</td>
<td>259 21,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenyl p-anisate (?)</td>
<td>p-Methoxy</td>
<td>261 22,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenyl p-nitrobenzoate (?)</td>
<td>p-Nitro</td>
<td>259 15,500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Nitrophenyl</td>
<td>p-Methoxy p-Nitro</td>
<td>276 27,400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-anisate (?)</td>
<td>p-Methoxy</td>
<td>228 19,400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Nitrophenyl</td>
<td>p-Nitro</td>
<td>266 20,600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-anisate (?)</td>
<td>p-Methoxy</td>
<td>261 23,500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-nitrobenzoate (?)</td>
<td>p-Nitro</td>
<td>258 15,500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Chlorophenyl</td>
<td>p-Chloro</td>
<td>249 22,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Iodophenyl</td>
<td>p-Iodo</td>
<td>260 22,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-Iodobenzoate</td>
<td>m-Methoxy</td>
<td>225 17,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-Anisyl m-anisate (?)</td>
<td>m-Methoxy</td>
<td>259 21,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Chlorophenyl benzoate</td>
<td>p-Chloro</td>
<td>232 17,500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Nitrophenyl</td>
<td>p-Nitro</td>
<td>257 20,000</td>
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<td></td>
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<tr>
<td>p-Chlorophenyl benzoate</td>
<td>p-Chloro</td>
<td>232 17,500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Iodophenyl</td>
<td>p-Iodo</td>
<td>260 22,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-Iodobenzoate</td>
<td>m-Methoxy</td>
<td>225 17,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-Anisyl m-anisate (?)</td>
<td>m-Methoxy</td>
<td>259 21,000</td>
<td></td>
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</tr>
<tr>
<td>m-Anisyl m-anisate (?)</td>
<td>m-Methoxy</td>
<td>273 3,000</td>
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<td></td>
</tr>
<tr>
<td>m-Chlorobenzoate</td>
<td>m-Chloro</td>
<td>260 22,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-Nitrobenzoate (7)</td>
<td>m-Methoxy</td>
<td>257 20,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Chlorophenyl benzoate</td>
<td>p-Chloro</td>
<td>232 17,500</td>
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</tr>
<tr>
<td>p-Nitrophenyl</td>
<td>p-Nitro</td>
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<td></td>
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</tr>
<tr>
<td>p-Iodophenyl</td>
<td>p-Iodo</td>
<td>233 23,800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexane ring</td>
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<td></td>
</tr>
<tr>
<td>Phenyl cyclohexanecarboxylate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Nitrophenyl</td>
<td>p-Nitro</td>
<td>268 10,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>phenyl cyclohexanecarboxylate</td>
<td></td>
<td>p-Methoxy</td>
<td>275 2,000</td>
<td></td>
</tr>
<tr>
<td>p-Anisyl cyclohexanecarboxylate</td>
<td></td>
<td>p-Methoxy</td>
<td>275 2,000</td>
<td></td>
</tr>
<tr>
<td>m-Anisyl cyclohexanecarboxylate</td>
<td></td>
<td>m-Methoxy</td>
<td>273 3,000</td>
<td></td>
</tr>
</tbody>
</table>
in the value and location of maximal absorption between a substituted benzoic acid and its phenyl ester is similar to, and roughly the same as between benzoic acid and phenyl benzoate; that is a wave-length shift of +3\(\mu\), and an intensity change of about +4,000. The greatest change is observed in the para-methoxy-compounds \((\Delta \lambda_{\text{max}} = 12\mu, \Delta \epsilon = 8,000)\), and this may be ascribed to a combination of favourable mesomeric and inductive effects, leading to an increased stabilisation of resonance types of type VI, i.e. a smaller energy difference between ground and excited states, and to increased probability of transition. The smallest change occurs in the para-nitro-compound \((\Delta \lambda_{\text{max}} = 1\mu)\) presumably because of the negative mesomeric effect of the nitro-group.

With a view to investigating the conjugation of non-bonding \(\pi\)-electrons of the oxygen-atom and the \(\pi\)-electrons of the B ring, a conjugation which Cilento considers to be rather weak, a number of esters were prepared in which this conjugation might be expected to manifest itself. Taking phenyl para-anisate as an example of a compound where conditions favouring this conjugation already exist, the introduction of a para-nitro-group into the B ring would be expected to enhance this effect; the nitro-group, by withdrawing electrons from the B ring, should stabilise excited states of type VI. This in fact occurs, and further bathochromic and hyperchromic shifts take place relative to phenyl \(p\)-anisate. (See table III). Cilento\(^{7}\) classifies this band
separately, but this seems to be unnecessary as it is apparently due to what is essentially the same type of transition. The introduction of a para-nitro-group into the B ring would generally be expected to give rise to a similar effect, and a second example is in fact provided by p-nitro-phenyl p-nitro benzoate, where bathochromic and hyperchromic shifts are again observed on comparison with the parent compound, that is, phenyl p-nitrobenzoate. In p-nitrophenyl p-nitrobenzoate the absorption due to ring B is not observed, since its maximal absorption closely approximates with that of the A ring (See Table III). This was confirmed by determining the maximal absorption of p-nitrophenyl cyclo-hexanecarboxylate, which, as expected, absorbs maximally in the same region (\( \lambda_{\text{max.}} \) 268 nm, \( \varepsilon_{\text{max.}} = 10,000 \)). Occasionally the ester spectrum exhibits the absorption due to ring B as an absorption maximum, but more often this appears as an inflection, as the intense A band partially masks the B band maximum.

Reversing the substituents in the above examples has the expected effect. A para-methoxy-group in the B ring, because of its mesomeric effect, causes a slight hypsochromic shift relative to phenyl benzoate. This is ascribed to the increased electron availability in the carboxyl-group which enhances the steric effect in that area. The expected hypsochromic shift is not observed as the increased absorption by the B ring (due to transitions of type VII) outweighs the supposed
intensity decrease which results from the slightly increased steric inhibition of resonance. A similar effect is observed in \(p\)-anisyl \(p\)-anisate, relative to phenyl \(p\)-anisate, and in \(p\)-anisyl \(p\)-nitrobenzoate relative to phenyl \(p\)-nitrobenzoate (See Table III). In B ring \(p\)-halogen substituted compounds an intermediate effect is observed; the \(para\)-halogen substituent does bring about a bathochromic shift, which is, however, smaller than that observed for a \(para\)-nitro substituent in the B ring. This fact is in accordance with the known mesomeric effects of the halogens, which lie between that of the nitro-group and that of the methoxyl-group.

\(meta\)-Substituents in the B ring produce a low intensity band in the 270 - 280\(\mu\) region. This band is not appreciably influenced by an unsubstituted A ring, as may be seen from the similar B ring absorption bands in the spectra of \(m\)-anisyl benzoate, and \(m\)-anisyl cyclohexanecarboxylate. However, if the A ring is so substituted that the main maximum occurs in the 250 - 260 region, the intensity at 270\(\mu\) due to this maximal absorption is great enough to mask the low intensity band due to B ring absorption.

Finally a number of other B ring substituted esters are listed in table III. In some instances the absorption due to ring A almost completely predominates, e.g. \(p\)-iodophenyl benzoate, while in others both A ring and B ring bands are of similar intensity, e.g. \(p\)-nitrophenyl benzoate.
PART I
THE OXIDATION OF ALCOHOLS
BY PHENYLHYDRAZINE AND SUBSTITUTED PHENYLHYDRAZINES

1. Historical introduction

Since its introduction by E. Fischer (1) osazone formation by oxidation with phenylhydrazine has been used extensively in the identification and characterisation of the monosacharoses. The formation of the osazone was ascribed by Fischer (1,2) to the oxidation of the originally formed saccharose phenylhydrazone to form a ketonic or aldehydic carbonyl group:

\[ \text{R.CHOH.CH} + \text{C}_6\text{H}_5.\text{NH}.\text{NH}_2 \rightarrow \text{R.CHOH.CH} = \text{N.NH.C}_6\text{H}_5 \]

\[ + \text{NH}_2.\text{NH.C}_6\text{H}_5 \]

\[ \text{R.CO.CH} = \text{N.NH.C}_6\text{H}_5 + \text{NH}_3 + \text{C}_6\text{H}_5.\text{NH}_2 \]

which then reacts with a third molecule of phenylhydrazine to yield the osazone. The quantitative isolation of the ammonia and aniline postulated to be formed in the reaction was not undertaken by Fischer.

In an attempt to examine the validity of Fischer's formulation of osazone formation, B. Blassman and Mrs. Rochwarz-Walbe (3) absorbed in permutite the ammonia formed in the reaction between sugars and phenylhydrazine in aqueous acetic acid at 100°. They found that the filtrate from the osazone contained more ammonia than was required by Fischer's mechanism and ascribed the excess to the decomposition of

1. Fischer, E. *Ber.* 17 579. (1884).
the phenylhydrazine:

\[ \text{C}_6\text{H}_5\text{NH} \cdot \text{NH}_2 \rightarrow \text{C}_6\text{H}_6 + \text{C}_6\text{H}_5\cdot \text{NH}_2 + \text{NH}_3 + \text{N}_2 \]

No alternative mechanism was proposed for the reaction.

It was found (4) that osazone formation appears to be completely inhibited if all external oxidising agents, including oxygen dissolved in water used for making up solutions, were rigorously excluded. This fact indicates that osazone formation is at least initiated by oxidising agents other than phenylhydrazine. No mention was made in this paper of whether hydrazone formation is similarly affected by the absence of oxygen, and no further mechanism was proposed for the oxidation reaction, or for the fact of its dependence on the presence of other oxidising agents.

Apart from its use in osazone formation, very few claims have appeared for the use of phenylhydrazine as an oxidising agent. In one of these, an investigation carried out by G. Oddo et al (5), it is claimed that phenylhydrazine will oxidise various alcohols at temperatures varying between 140 and 190°. The procedure adopted by Oddo was to mix about 0.5 g of the alcohol with about 1.0 g of phenylhydrazine in a test tube, which was then immersed in an oil bath at the appropriate temperature.

5. G. Oddo and A. Goacalone Gazz chim Ital. 298. (1928).
In the case of benzyl alcohol a yield of 30% was recorded after three hours at 190°. In several attempts to repeat this I have obtained either no yield, or less than 0.1%. (see experimental). Oddo also claims to have oxidised salicyl alcohol to salicylaldehyde phenylhydrazone in 15 minutes at 140°. Under similar conditions, I have obtained a small yield (ca 5%) of salicylaldehyde phenylhydrazone, together with two other compounds which have not yet been identified (See experimental).

The one with melting point 101.5° is unstable, decomposing to a dark oil in two to six days; consequently no reliably elemental analysis is available for this compound. The other compound melts at 152° and is quite stable. Elemental analysis shows it to have empirical formula C10H10O4. In connection with these two compounds, it is interesting to note that various workers (6; 7) have reported addition products of phenylhydrazine with phenols under the conditions given by Oddo. A further point of interest is that at the temperature of these reactions phenylhydrazine decomposes to yield \( \alpha,\alpha \)-diphenyl-hydrazine and aniline, both of which are presumably capable of forming adducts with phenols such as salicyl alcohol.

Finally, in connection with the supposed oxidising power of

6. R. Cuisa and A. Bernardi  Gazz. chim Ital. 40 11 158
7. R. Cuisa and A. Bernardi  Atti. acad. Lincei. 22 1 690
phenylhydrazine, F. Robinson (8) reports that titanous chloride is without effect on phenylhydrazine and p-bromophenylhydrazine, but that it reduces p-nitro-phenylhydrazine to p-phenylene diamine and ammonia.

F. Weygand (9), in order to account for the above observations, and to correlate his own observation that 1-(N-aryl-) fructoses also form osazones - often in better yield than the parent sugar - has proposed a new mechanism for the oxidation involving the Amadori rearrangement. This is illustrated below for the formation of the phenylhydrazone of an aldose.

\[ \text{Aldose} \quad \xrightarrow{\text{HC:N.NH.Ph}} \quad \text{HC=NH.NH.Ph} \quad \xrightarrow{\text{HC:NH,NH.Ph}} \quad \text{HC-NH,NH.Ph} \]

\[ \text{H} \_2 \text{N.NH.Ph} \]

\[ \text{HC:N,H.NH.Ph} \]

\[ \text{C:N.H.NNH.Ph} \]

\[ \xleftarrow{\text{-HCOH}} \]

\[ \text{HC:NH} \]

\[ \text{C:O} \]

\[ + \text{NH}_3 + \text{H}_2\text{O} \]

The present investigation arises from the observation (10) that Brady's reagent will react with certain alcohols to yield the 2,4-dinitrophenylhydrazone of the corresponding aldehyde or ketone. Braude and Forbes propose a mechanism to explain this reaction, and also extend the concept to osazone formation from \( \alpha \)-keto-alcohols.

9. F. Weygand Ber. 73 1248 (1940)
The initial step is postulated to be the formation of a hydrogen-bonded complex (1) which afterwards decomposes in the manner shown.

\[
\begin{align*}
X-\text{CHOH} + \text{Ar.NH}_2 & \rightarrow X-\text{C}=\text{H} & \rightarrow X-\text{C}=\text{O} + \\
Y & & \text{Y} \rightarrow \text{NH}_2 \text{Ar} & & \text{NH}_4 \text{Ar}.
\end{align*}
\]

This mechanism explains requirements of acid conditions as well as of electron recession at the hydrazone-group. It also correlates the formation of osazones with the oxidation of unsaturated alcohols by phenylhydrazines. In osazone formation, \(X\) represents the grouping \(\text{CH}=\text{N.NH.A}r\). For unsaturated alcohols, \(X\) represents \(\text{CH}=\text{C}_{3}\text{B} \) or \(\text{C}_6\text{H}_5\).

The purpose of the present investigation has been to establish the mechanism proposed above by attempting to isolate the \(\text{Ar.NH}_2\) which is postulated to have been formed during the reaction; and, by quantitatively comparing reaction rates and percentage yields under standard conditions to establish the effect of the nature of \(X\), \(Y\), and \(\text{Ar}\) on the rate of the reaction. An examination of the reactions described by Oddo (5) was also undertaken and this work extended to \(\text{p}-\text{nitro}\)- and \(2,4\)-dinitrophenyl-hydrazines.
TABLE I
OXIDATION OF ALCOHOLS BY 2,4-DINITROPHENYLHYDRAZINE
UNDER STANDARD CONDITIONS
ACCORDING TO BRAUDE AND FORBES (10)

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Yield of derivative</th>
<th>Reaction time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crotyl alcohol</td>
<td>0%</td>
<td>5 hours</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>0%</td>
<td>5 hours</td>
</tr>
<tr>
<td>Diphenylmethyl alcohol</td>
<td>4%</td>
<td>1 hour</td>
</tr>
<tr>
<td>Cinnamyl alcohol</td>
<td>10%</td>
<td>1 hour</td>
</tr>
<tr>
<td>Sorbyl alcohol</td>
<td>10%</td>
<td>5 minutes</td>
</tr>
<tr>
<td>4-cyclo-Hex-1'-enylbut-3-en-2-ol</td>
<td>10%</td>
<td>5 minutes</td>
</tr>
<tr>
<td>4-cyclo-Hept-1'enylbut-3-en-2-ol</td>
<td>10%</td>
<td>5 minutes</td>
</tr>
<tr>
<td>2-Benzylidencyclopentanol</td>
<td>20%</td>
<td>5 minutes</td>
</tr>
<tr>
<td>4-Phenylbut-3-en-2-ol</td>
<td>25%</td>
<td>5 minutes</td>
</tr>
<tr>
<td>Vitamin A₁</td>
<td>15%</td>
<td>5 minutes</td>
</tr>
</tbody>
</table>

TABLE II
OXIDATION OF ALCOHOLS BY PHENYLHYDRAZINES

<table>
<thead>
<tr>
<th>Phenylhydrazine</th>
<th>Cinnamyl Alcohol</th>
<th>Salicyl Alcohol</th>
<th>Benzy1 Alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yield</td>
<td>Time</td>
<td>Yield</td>
</tr>
<tr>
<td>Pheny1hydrazine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0%</td>
<td>2 hours</td>
<td>5%</td>
</tr>
<tr>
<td>B</td>
<td>0%</td>
<td>1 hour</td>
<td>0%</td>
</tr>
<tr>
<td>p-Nitrophenylhydrazine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0%</td>
<td>1 hour</td>
<td>50%</td>
</tr>
<tr>
<td>B</td>
<td>0%</td>
<td>1 hour</td>
<td>0%</td>
</tr>
<tr>
<td>2,4-Dinitrophenylhydrazine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>10%</td>
<td>7 hours</td>
<td>*</td>
</tr>
<tr>
<td>B</td>
<td>10%</td>
<td>1 hour (10)</td>
<td>0%</td>
</tr>
<tr>
<td>2,4,6-Trinitrophenylhydrazine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>*</td>
<td>3 to 18</td>
<td>+</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>hours</td>
<td>+</td>
</tr>
</tbody>
</table>

A Conditions described by Oddo et al (5)
B Conditions described by Braude and Forbes (10)
* Reaction occurs but the product is not the required phenylhydrazone
† Reaction not performed
2. Discussion

The results shown in table I indicate that if \( Y = \text{H} \) or a saturated carbon-atom, then unsaturation in \( X \) such that the newly formed carbonyl-group would be conjugated with \( X \), tends to increase the rate of reaction. Furthermore, the reaction mechanism under investigation suggests that the reaction might proceed considerably more readily with a hydrazine derivative such as 2,4,6-trinitrophenylhydrazine; i.e., one which is more highly substituted in the benzene-ring with electron attracting groups. Accordingly, two sets of reactions were performed with each alcohol/phenyl-hydrazine pair. Each pair was heated in aqueous ethanolic sulphuric acid solution and also by oil bath immersion as described by Oddo (5) (See experimental). The results are recorded in table two. These results suggest that the mechanism of reaction is not the same in both sets of conditions. A comparison with table I shows that for oxidation in solution an ethylenic bond appears to have a greater activating effect than a phenyl-group. That this is so is easily seen from a comparison of cinnamyl alcohol with vitamin A\(_1\). This fact is not immediately explicable by any of the mechanisms so far proposed.

Apart from the reactions with salicyl alcohol, which must be regarded as special cases involving the phenolic function in some way, the reactions in the absence of solvent are of little immediate interest.
The small amount of oxidation product obtained by the action of 2, 4-dinitrophenylhydrazine on cinnamyl and benzyl alcohols may be attributed to atmospheric oxidation of the alcohol, especially as it has been shown (see experimental) that benzyl alcohol is oxidised in the air at 180°, the extent of reaction after 7 hours being approximately 3%. These reactions seem to bear little relationship with the reactions in acidic solution described by other workers, and the general application of phenylhydrazines to the oxidation of alcohols in the absence of a solvent is rendered even less probable when it is remembered that phenylhydrazine itself is a strong reducing agent, reducing N=N bonds to N-N (11).

In the formulation of a mechanism to explain the oxidation of alcohols in acid solution there are six points to consider. Firstly, although all mechanisms so far proposed, postulate the formation of a free carbonyl-group at one stage in the reaction, and the formation of Ar. NH₂ has been demonstrated in the case of \( \alpha \)-keto-alcohols, no Schiff's base of the form \[ \begin{array}{c} \ X \\ \ Y \end{array} \ C=\text{N} \text{Ar} \] has ever been isolated from one of the reactions. This is strong evidence that at no time during the reaction is a free carbonyl-group present, and suggests that in the initial stages of the reaction the phenylhydrazine molecule attaches

itself directly to the carbon-atom being oxidised, and that the final, and probably the rate determining step is the loss of water from a compound of type \( \text{II} \).

\[
\begin{align*}
\text{I} & : \quad C' \text{OH} \\
\text{II} & : \quad Y \text{NH.NH.Ar}
\end{align*}
\]

The other points to bear in mind when formulating a mechanism for this reaction are:

One: Phenylhydrazines have never been used as oxidising agents except in the special case of \( \alpha \)-keto alcohols and \( \beta \gamma \)-unsaturated alcohols.

Two: Phenylhydrazines will not oxidise such a powerful inorganic reducing agent as titanous chloride (8).

Three: Phenylhydrazine has been used as a powerful reducing agent, and reduces \(-N=N-\) double bonds so vigorously that the reaction tends to become explosive (11), and also reduces such weak inorganic oxidising agents as \( \text{Cu}^{2+} \) (12); a reduction which \( \beta \gamma \)-unsaturated alcohols and \( \alpha \)-keto-alcohols do not perform.

Four: The possible dependence of the reaction on the presence of molecular oxygen.

Five: The necessity for acid conditions.

This last condition appears to be very variable. For instance it has

been shown (13) that a strong mineral acid, e.g., HCl is not such an
effective catalyst for osazone formation as is a weak acid at the same
pH, both H$_3$PO$_4$ and acetic acid have been used. However, in the
oxidation of $\beta\gamma$-unsaturated alcohols, acetic acid will not catalyse
the reaction at all (10). This fact, coupled with the observation
(See experimental) that no 2,4-dinitroaniline was found among the
reaction products of cinnamyl alcohol with 2,4-dinitrophenylhydrazine,
suggests that the mechanism operating in osazone formation is not
necessarily the same as the mechanism of the oxidation of $\beta\gamma$-unsaturated
alcohols.

The possible dependence on the presence of molecular oxygen suggests
the possibility of a free radical mechanism for this reaction, and the
greater activating power of ethylenic bonds suggests a similarity in
the initial stages to the auto-oxidation of the Olephines. A further
point in favour of the free radical mechanism is the observation (10)
that secondary alcohols are more easily oxidised than are primary
alcohols, while under normal conditions the reverse is true. This
observation is evidence that the rate determining step is a dehydration
rather than a dehydrogenation.

Although there is no direct evidence of the presence of free
radicals in these reactions, this explanation of the abnormal oxidising
power of phenylhydrazine under these highly specialised conditions is
more satisfactory than one which involves the intermediate formation of
a free carbonyl-group in the same solution as a primary aromatic amine,
while no Schiff's bases are to be found in the reaction products.
PART III
EXPERIMENTAL

The ultraviolet absorption spectra were determined in duplicate by standard methods using a Unicam SP500 spectrophotometer.

Melting points are uncorrected; analyses were carried out in the micro-analytical laboratory (Mr. F.H. Oliver) of the department of Organic Chemistry, Imperial College, London, England, and in the micro-analytical laboratory (Mr. A. Bernhardt) of the Max-Planck Institut für Kohlenforschung, Mülheim, Ruhr, Germany.

Benzoic Acids

The commercially available compounds were crystallised to constant melting point and intensity of absorption. o-Fluoro-, m-fluoro-, p-bromo-, and m-nitrobenzoic acids were obtained by the oxidation of the appropriate toluene according to the method described by Vogel (1).

p-Bromo-benzoic acid had melting point 251 - 253°. (Heilbron and Bunbury (2) give melting point 251 - 253°) Anal.: Calc. for C₇H₅O₂Br: Br, 39.75%. Found: Br, 40.1%. Light absorption in ethanol: see part I, table I.

Phenyl Benzoates

The esters were prepared by standard methods. Solid esters were crystallised to constant melting point and intensity of absorption;

liquid esters were distilled to constant refractive index and intensity of absorption.

Phenyl benzoate crystallised as prisms, melting point 70° (Heilbron and Bunbury (2) give melting point 71°); phenyl p-chlorobenzoate crystallised as plates, melting point 100° (Birkenbach and Meisenheimer (3) give melting point 100°); phenyl p-iodobenzoate crystallised as plates, melting point 133°. Anal.: Calc. for C\(_{13}H_9O_2I\): C, 48.2; H, 2.8; I, 39.1%. Found: C, 47.9; H, 2.6; I, 39.0%. p-Chlorophenyl p-chloro-benzoate crystallised as plates, melting point 71° (Birkenbach and Meisenheimer (3) give melting point 71°); p-iodophenyl p-iodobenzoate crystallised as plates, melting point 143°. Anal.: Calc. for C\(_{13}H_9O_2I_2\): C, 34.7; H, 1.8; I, 56.4%. Found: C, 34.7; H, 2.1; I, 56.1%. m-Anisyl benzoate distilled at 163°, 3mm., n\(_D\) 1.5751. Anal.: Calc. for C\(_{14}H_{12}O_3\): C, 73.7; H, 5.3%. Found: C, 73.9; H, 5.5%. m-Anisyl p-anisate crystallised as prisms, melting point 102°. Anal.: Calc. for C\(_{15}H_{14}O_4\): C, 69.75; H, 5.5%. Found: C, 69.95; H, 5.7%. m-Anisyl p-nitro-benzoate crystallised as needles, melting point 126°. Anal.: Calc. for C\(_{14}H_{11}O_2N\): C, 61.5; H, 4.1; N, 5.1%. Found: C, 61.4; H, 4.3; N, 4.9%. p-Chlorophenyl benzoate crystallised as needles, melting point 87° (Autenrieth and Millinghaus (4) give melting point 86°); p-iodophenyl benzoate crystallised as needles, melting point 119° (Willgerodt and Wiegand (5) give melting point 118.5° - 119.5°).

The light absorption properties of the above described compounds are recorded in Table III of part I.

W. Autenrieth and P. Millinghaus Ber. 39:102. (1906)
5. C. Willgerodt and G. Wiegand Ber. 42:3768. (1909)
Phenyl Cyclohexanecarboxylates

Cyclohexanecarboxylic acid was prepared from cyclohexyl chloride according to the method of Gillman and Zoellner (6) and distilled at 179°, 17 mm.; \( n_D^{30} 1.4620 \) as a colourless liquid, which solidified on standing to a solid, melting point 28° (Hiers and Adams (7) give boiling point 105°, 4 mm \( n_D^{28} 1.4520 \); melting point 29 – 30°). The esters were prepared in the above described manner.

Phenyl cyclohexanecarboxylate distilled at 129°, 3 mm. \( n_D^{27} 1.5107 \).

Anal.: Calc. for \( C_{13}H_{16}O_2 \): C, 76.4; H, 7.9%. Found: C, 76.5; H, 8.0%.

p-Nitrophenylcyclohexanecarboxylate crystallised as needles, melting point 53.5°. Anal.: Calc. for \( C_{13}H_{15}O_4N \): C, 62.6; H, 6.1; N, 5.6%. Found: C, 62.3; H, 5.9; N, 5.7%.

p-Anisyl cyclohexanecarboxylate crystallised as needles, melting point 64°. Anal.: Calc. for \( C_{14}H_{18}O_3 \): C, 71.8; H, 7.7%. Found: C, 71.5; H, 7.8%. m-Anisyl cyclohexanecarboxylate distilled at 80°, 3 mm., \( n_D^{28} 1.5460 \). Anal.: Calc. for \( C_{14}H_{18}O_2 \): C, 71.8; H, 7.7%. Found: C, 72.0; H, 7.9%.

The light absorption properties of the above described compounds are recorded in Table III of part I.

The reactions of alcohols with phenylhydrazine and with substituted phenylhydrazines at high temperatures

In each of the following reactions, 0.005 moles of the alcohol was intimately mixed with 0.01 moles of the phenylhydrazine in a test tube, which was then immersed in an oil bath at the stated temperature for the appropriate length of time. Reaction products were worked up as indicated.

**Salicyl alcohol and phenylhydrazine**

After 15 minutes at 140° the reaction mixture was cooled to room temperature. In some of the runs the mixture solidified, especially if allowed to stand over night, but in the majority of cases a very viscous light brown oil was obtained. This was dissolved in its own volume of ethanol with warming. Addition of water dropwise to the cooled solution resulted in a sudden heavy precipitation. The solution was then filtered with suction. The residue was a sticky yellow solid which crystallised as white needles from methanol, melting point 101.5°. This substance slowly decomposed at room temperature to a dark brown oil. Anal.: Calc. for C_{13}H_{16}O_{2}N_{2}: C, 67.2; H, 6.9; N, 12.1%. Found: C, 68.8; H, 6.6; N, 11.5%. The formula C_{13}H_{16}O_{2}N_{2} corresponds to a compound with structure I.

\[ \text{I: } \]

\[
\text{C}_{13}\text{H}_{16}\text{O}_{2}\text{N}_{2}
\]
A rapid stream of air was blown over the surface of the filtrate from this reaction. As the ethanol evaporated a second solid was precipitated. This crystallised as plates from methanol, melting point $152^\circ$. Anal.: Calc. for $\text{C}_{19}\text{H}_{20}\text{O}_{2}\text{N}_2$: C, 74.1; H, 6.5; N, 9.1%. Found: C, 74.3; H, 6.5; N, 8.8%. The formula $\text{C}_{19}\text{H}_{20}\text{O}_{2}\text{N}_2$ corresponds with a compound of structure II.

![Structure II](image)

The yields of these two substances, based on the amount of alcohol used were each about 40%.

In some runs a small amount of salicylaldehyde phenylhydrazone was precipitated together with the second substance. The two compounds were separated by fractional crystallisation from methanol. The phenylhydrazone was identified by its mixed melting point ($142^\circ$) with an authentic sample. The maximum yield of the phenylhydrazone was 5% based on the amount of alcohol used. Increasing the incubation period to up to an hour did not materially increase the yield of any of the products, and the reaction is apparently over in the first fifteen minutes.

**Benzyl Alcohol and phenylhydrazone**

After three hours at $190^\circ$ the reaction mixture was cooled to room temperature. Addition of an equal volume of 50% ethanol produced no
change in the dark oily reaction product, except in one case, where a
very faint precipitate appeared. This was filtered off, and subsequently
identified by its melting point and mixed melting point (158°) as
benzaldehyde phenylhydrazone. The yield in this case was 0.1% based on
the weight of alcohol used. In no other case was any solid product
isolated. It has been shown (See below) that benzyl alcohol is oxidised
by the air at 190° and the nonappearance of any benzaldehyde phenylhydra-
zone suggests that the phenylhydrazone might in fact be preventing the
atmospheric oxidation which otherwise would take place.

Cinnamyl alcohol and phenylhydrazone

The reaction mixture was heated at 150° - 180° for periods of time
from fifteen minutes to two hours. No solid product could be isolated
from any of the reaction mixtures.

Salicyl alcohol and p-nitrophenylhydrazone

Salicyl alcohol (1.1g., = 0.01 moles) and p-nitrophenylhydrazone
(1.5g., = 0.01 moles) were intimately mixed in a test tube which was
then immersed in an oil bath at 145° for thirty minutes. During this
time the mixture at first melted and then resolidified after twenty-
five minutes. The cooled reaction mixture was washed with ether. The
solution on evaporation yielded a dark tar. The residue, (0.8g)
crystallised from methanol as plates, melting point 227°. Mixed melting
point with an authentic specimen of salicyl aldehyde p-nitrophenylhydra-
zeone 229°.

No other solid product could be isolated from this reaction.
Benzyl alcohol and p-nitrophenylhydrazine

The reaction mixture was heated at 140° for one hour. At the end of this time, 95% of the alcohol was recovered by steam distillation. The non-steam volatile residue was washed with ether, when a small amount of a dark tar dissolved. The residue had melting point 158 - 161°. Mixed melting point with p-nitrophenylhydrazine 159 - 161°. This solid was chromatographed on a column of "Light's" Alumina using chloroform as solvent and ethyl acetate as developer. Only one band was observed.

Cinnamyl alcohol and p-nitrophenylhydrazine

The reaction mixture was heated at 145° for one hour. It was then worked up in the above described manner. 85% of the cinnamyl alcohol was recovered. Rather more tar was obtained, and the residue was once again almost pure p-nitrophenylhydrazine.

Salicyl alcohol and 2,4-dinitrophenylhydrazine

After six minutes immersion in an oil bath at 145° this reaction mixture began to effervesce. After fifteen minutes the effervescence had ceased, although the mixture was still liquid. After twenty minutes a very violent decomposition of the mixture occurred, with evolution of gas. If the test tube was removed from the heat after fifteen minutes and cooled rapidly, a dark red glass was left as the product. This was almost entirely soluble in hot methanol. The insoluble residue, amounting to less than 5% of the total reaction mixture, was identified by its melting point and mixed melting point with an authentic sample as salicylaldehyde 2,4-dinitrophenylhydrazone. The hot methanolic solution
deposited crystals on cooling. These were red in colour, and this substance crystallised from methanol as needles, melting point 202°. Mixed melting point with 2,4-dinitrophenylhydrazine 185 - 189°. This substance was not submitted for analysis.

**Benzyl alcohol and 2,4-dinitrophenylhydrazine**

The mixture was heated at 190° for seven hours. At the end of this period, 85% of the benzyl alcohol was recovered by steam distillation. The residue was washed with ether to remove a dark tar, and then chromatographed on a column of "Light's" alumina using chloroform as solvent, and benzene as developer. One band was eluted in this fashion, while another remained on the column. When the eluate was taken to dryness a red solid remained. This was crystallised from ethyl acetate. It was obtained as needles, melting point 237°. Mixed melting point with an authentic sample of benzaldehyde 2,4-dinitrophenylhydrazone 236°. Yield 2 - 5%.

**Cinnamyl alcohol and 2,4-dinitrophenylhydrazine**

The mixture was heated at 150° for seven hours, and then was worked up in the above described manner. 70% of the cinnamyl alcohol was recovered by steam distillation, and rather more tar was obtained. The cinnamaldehyde 2,4-dinitrophenylhydrazone was identified by its melting point and mixed melting point with an authentic sample. Melting point and mixed melting point 250°. Yield 5 - 10%.
The reactions of alcohols with phenylhydrazine and with substituted phenylhydrazines in acidic solution

In all the following reactions, approximately 1g. of the alcohol was treated with a 3 - 5 molar excess of the reagent made up as described below. The reaction in all cases was carried out at 60° under an inert atmosphere. Heating, unless otherwise indicated, was prolonged for one hour.

In the case of cinnamyl alcohol with 2,4- and 2,6-nitrophenylhydrazines, a precipitate appeared during the course of the reaction. In none of the other reactions was any change noted.

Cinnamyl alcohol and 2,4-dinitrophenylhydrazine

1g. of cinnamyl alcohol was dissolved in 100mls. of Brady's reagent (See below) and the mixture heated under an inert atmosphere at 60° on a water bath. The temperature of the mixture was indicated by a thermometer immersed in it. After one hour a small precipitate had appeared.

The mixture was cooled and filtered. The residue weighed 0.2g. and had melting point after one crystallisation from ethyl acetate of 249 - 250°.

Mixed melting point with an authentic sample of cinnamaldehyde 2,4-dinitrophenylhydrazone 250°. Thus the 10% yield reported earlier (10) was confirmed. The filtrate was then steam distilled. The distillate was ether extracted. Drying of the ether layer, followed by removal of the ether left an oil which distilled at 70°, 3mm. nD 1.5730. Cinnamyl alcohol has boiling point 112°, 12mm. nD 1.5820. Anal: Cal. for C9H10O: C, 80.7; H, 7.5%. Found: C, 80.2; H, 8.4%. These values suggest that this oil might be cinnamyl alcohol. Further evidence of this
was obtained from the ultraviolet absorption spectrum, which closely resembled that of cinnamyl alcohol. No other product was isolated from this reaction.

**Cinnamyl alcohol and 2,4,6-trinitrophenylhydrazine**

1g. cinnamyl alcohol was dissolved in the reagent and the mixture heated on a water bath for up to 18 hours. Any ethanol lost during this period was made up and the mixture filtered from the small amount of tar which appeared during course of the reaction. The filtrate was diluted with its own volume of water. A yellow precipitate slowly appeared. Longer periods of heating increased the yield of this product. It crystallised from aqueous ethanol as needles, melting point 128°. No reliable analysis is available for this compound. As approximate analysis shows the following percentages of the elements. C, 38.5 - 40.0%, H, 3.2 - 5.2%, N, 22.8 - 24.7%. No sulphur was found in the compound.

The filtrate was extracted with chloroform to remove any unreacted alcohol, and then with ether. The ether layer was dried and the ether removed, leaving a brown solid which crystallised from glacial acetic acid as needles, melting point 202°. This compound had a molecular weight of 273 (Bast). Anal.: C, 32.7%; H, 1.5%; N, 30.3%. No molecular formula can be written corresponding with these values.

No cinnamaldehyde 2,4,6-trinitrophenylhydrazone was obtained from this reaction.

**Preparation of reagents**

1. **Phenyldrazine and p-nitrophenylhydrazine**

Phenyldrazine or p-nitrophenylhydrazine (4g.) was dissolved in 60mls. ethanol. 8mls. of concentrated sulphuric acid was diluted to 200mls. and
added to the above solution.

2. 2,4-Dinitrophenylhydrazine

Brady's reagent was prepared according to the method described by Braude and Forbes (10).

3. 2,4,6-trinitrophenylhydrazine

2,4,6-Trinitrophenylhydrazine, prepared according to the method of Batal (8) was dissolved in concentrated sulphuric acid (2.4g.). 40mls. of ethanol were added slowly with cooling. The mixture was boiled and filtered hot. 10 mls of water and a further 60mls of ethanol were added to the filtrate.

The atmospheric oxidation of benzyl alcohol

Benzyl alcohol (5g.) was placed in a test tube which was immersed in an oil bath at 190°. These conditions were maintained for 7 hours. The alcohol was then treated with an excess of brady's reagent, when an immediate precipitation of benzaldehyde 2,4-dinitrophenylhydrazone occurred. The weight of this precipitate was 0.45g. It crystallised from ethyl acetate as needles, melting point and mixed melting point 237°.
