LXX.—*Derivatives of p-Hydroxystilbene.*

By JOHN THEODORE HEWITT, WILLIAM LEWCOCK, and
FRANK GEORGE POPE.

As a result of spectrographic measurements, it has been shown that the addition of alkali to an alcoholic solution of an azophenol produces a displacement of the selective absorption to the red end of the spectrum (Tuck, Trans., 1907, **91**, 449; 1909, **95**, 1809); the displacement of the absorption is, however, far greater in the case of *p*-nitrobenzeneazophenol than in that of benzeneazophenol itself (Hewitt and Mitchell, Trans., 1906, **89**, 13, 17; 1907, **91**, 1251; Baly, Tuck, and Marsden, Trans., 1910, **97**, 1494). Hewitt and Mitchell suggest that the difference is due to the salts of *p*-nitrobenzeneazophenol possessing a quinonoid structure:

from this view Baly, Tuck, and Marsden dissent.

It has been shown (F. G. Pope, Trans., 1908, **93**, 532) that whilst the condensation product of benzaldehyde and *p*-aminophenol gives faintly yellow alkaline solutions, the corresponding alkaline solutions of *p*-nitrobenzylidene-*p*-aminophenol are deep orange-red; in this case the formation of a quinonoid salt has been suggested. Evidently the replacement of one nitrogen atom in the azophenols by a methine group involves a higher oscillation frequency of the molecule; but the same sort of shift is produced on adding alkali to benzylidene-*p*-aminophenol as that which occurs with benzeneazophenol, and in both cases the presence of a *p*-nitro-group conditions a greater displacement of the absorption when alkali is added. In

these circumstances it appeared desirable to examine the corresponding stilbene compounds so as to complete the series:

EXPERIMENTAL.

In preparing the materials necessary for this work, syntheses from phenylacetic acid and its *p*-nitro-derivative with suitable aldehydes were employed. Walther and Wetzlich (*J. pr. Chem.*, 1900, [ii], **61**, 181) obtained α -*p*-nitrophenylcinnamic acid by heating *p*-nitrophenylacetic acid and benzaldehyde to 205°, but were unable to effect a smooth removal of carbon dioxide; many syntheses of phenanthrene derivatives in which stilbene compounds are intermediately formed have been carried out by R. Pschorr (*Ber.*, 1900, **33**, 176, etc.), who follows Perkin's synthesis of cinnamic acid in that he heats the sodium salt of the substituted phenylacetic acid with the necessary aldehyde and acetic anhydride. During the progress of the present work a paper appeared by Pfeiffer and Sergiewskaja (*Ber.*, 1911, **44**, 1107), in which the condensation of aldehydes and substituted phenylacetic acids was effected by piperidine, and of this reaction we have made considerable use. It is noteworthy that whilst Walther and Wetzlich employed a temperature of 205° to effect the condensation of *p*-nitrophenylacetic acid and benzaldehyde, addition of piperidine causes reaction to take place at 150–160°, and, moreover, effects the removal of carbon dioxide, so that Pfeiffer and Sergiewskaja isolated quite fair yields of nitrostilbene.

p-Hydroxystilbene, $\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$.—Five grams of *p*-hydroxybenzaldehyde, 5 grams of phenylacetic acid, and 1 c.c. of piperidine were heated for five hours to 150°. From the resulting product, unchanged phenylacetic acid was extracted by hot dilute sodium carbonate solution, and the residue was dissolved in hot dilute aqueous sodium hydroxide; on cooling, the colourless, crystalline sodium salt of hydroxystilbene was deposited. This salt separates readily from its solutions on addition of sodium hydroxide; the free hydroxystilbene was liberated by dilute hydrochloric acid, and crystallised from dilute alcohol:

0.1193 gave 0.3746 CO_2 and 0.0656 H_2O . $\text{C}=85.6$; $\text{H}=6.1$.

$\text{C}_{14}\text{H}_{12}\text{O}$ requires $\text{C}=85.7$; $\text{H}=6.1$ per cent.

This substance is a colourless, crystalline powder, which melts at 184.5° (uncorr.), and is readily soluble in alcohol; the solution in concentrated sulphuric acid is red.

p-Methoxystilbene, $C_6H_5 \cdot CH : CH \cdot C_6H_4 \cdot O \cdot CH_3$.—Oglialoro obtained this compound from the corresponding carboxylic acid by distillation (*Jahresber.*, 1879, 731); Funk and von Kostanecki eliminated carbon dioxide by allowing the acid to remain for some days with hydriodic acid (D 1.96) in the cold (*Ber.*, 1905, 38, 940). It has now been found that piperidine may be used for effecting removal of carbon dioxide from the carboxylic acid; heating in this case is more prolonged than if the piperidine is simply to be used for condensation of anisaldehyde and phenylacetic acid. When piperidine is employed, purification of the product can be effected by dissolving the crude product in hot light petroleum; on cooling, tarry matter is first deposited, and is fractionally removed. Repeating this process several times and finally crystallising from alcohol gives a product melting at 136° , as observed by Oglialoro; the compound is very soluble in hot alcohol, but separates nearly completely on cooling.

Methoxystilbene can also be prepared from hydroxystilbene by dissolving it in dilute alkali and warming gently with methyl sulphate. Probably Oglialoro's method is the most convenient; it is simple, and gives reasonable yields.

Methoxystilbene resembles hydroxystilbene in giving a red coloration with concentrated sulphuric acid; possibly quinonoid oxonium salts:

corresponding with the salts of the azophenols with mineral acids, are produced.

*α -Phenyl-*p*-methoxycinnamic Acid,*

—Oglialoro condensed anisaldehyde and phenylacetic acid, using Perkin's method; piperidine can, however, be conveniently employed. One c.c. of piperidine is added to 10 grams of an equimolecular mixture of anisaldehyde and phenylacetic acid; after heating for three hours at 150° , the mass solidifies on cooling. Washing with cold glacial acetic acid removes tarry impurities; a solution of the residue in hot alcohol deposits *α -phenyl-*p*-methoxycinnamic acid* in colourless needles on cooling. (Found, $C=75.1$; $H=5.6$. Calc., $C=75.4$; $H=5.5$ per cent.)

p-Nitrostilbene.—The requisite material was prepared by the method of Pfeiffer and Sergiewskaja (*loc. cit.*, 1109); the specimen used melted, in agreement with their determination, at 155° .

p-Nitro-*p'*-hydroxystilbene, $NO_2 \cdot C_6H_4 \cdot CH : CH \cdot C_6H_4 \cdot OH$.—This compound was obtained by boiling *α -p-nitrophenyl-*p*-acetoxycinnamic acid* with equal volumes of alcohol and fuming hydrochloric acid for four hours under reflux; not only was the acetyl group hydro-

lysed, but carbon dioxide was also eliminated from the carboxyl group. The alcoholic solution was poured into water, and the resulting precipitate crystallised from dilute alcohol, when it formed yellow needles melting at 193° (uncorr.):

0.1146 gave 0.2943 CO_2 and 0.0439 H_2O . $\text{C}=70.0$; $\text{H}=4.2$.

0.1414 „ 7.4 c.c. N_2 at 17.5° and 760 mm. $\text{N}=6.0$.

$\text{C}_{14}\text{H}_{11}\text{O}_3\text{N}$ requires $\text{C}=69.7$; $\text{H}=4.6$; $\text{N}=5.8$ per cent.

A good yield of the compound may also be obtained by Pfeiffer's method; the reaction product is dissolved in hot glacial acetic acid, from which solution cold water precipitates the nitrohydroxystilbene. The substance is subsequently crystallised from dilute alcohol or xylene.

Nitrohydroxystilbene dissolves in alcohol with a pale yellow colour; addition of alkali to the solution makes it assume a deep brown shade. Attempts to methylate an alkaline solution by methyl sulphate were unsuccessful, although the conditions were similar to those obtaining when hydroxystilbene was successfully methylated.

α -p-Nitrophenyl-p-acetoxycinnamic Acid,

—Eighteen grams of *p*-nitrophenylacetic acid were dissolved in 100 c.c. of *N*-sodium hydroxide, the solution evaporated to dryness, and the residual salt boiled for eight hours with 12 grams of *p*-hydroxybenzaldehyde and 50 grams of acetic anhydride (temperature of oil-bath 170°). The mass was extracted by boiling with dilute alcohol (three hours), the solution poured into water, and the precipitate allowed to settle; this takes some time. From the precipitate the acid was extracted with sodium carbonate solution, reprecipitated with hydrochloric acid, and crystallised from a mixture of carbon tetrachloride and glacial acetic acid. It forms a pale yellow, crystalline powder, melting at 205° (uncorr.):

0.0883 gave 0.2009 CO_2 and 0.0285 H_2O . $\text{C}=62.1$; $\text{H}=3.7$.

$\text{C}_{17}\text{H}_{13}\text{O}_6\text{N}$ requires $\text{C}=62.4$; $\text{H}=3.9$ per cent.

p-Nitro-p'-methoxystilbene, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_3$.—Elimination of carbon dioxide by heating the corresponding carboxylic acid with 66 per cent. sulphuric acid gives a poor yield, much of the substance being charred; similar results were obtained on boiling with concentrated hydrochloric acid. A small yield is also obtained when the acid is heated above its melting point; the reaction gives a somewhat better result when the acid is distilled under diminished pressure. It may be noticed that Walther and Wetzlich (*loc. cit.*) were unable to obtain nitrostilbene from the corresponding carboxylic acid.

Pfeiffer's method gives a good yield of pure material. Eight grams

of nitrophenylacetic acid, 6 grams of anisaldehyde, and 2 c.c. of piperidine were heated for four hours at 150—170°; any unaltered material was extracted with hot dilute sodium hydroxide, the residue dissolved in hot glacial acetic acid, and on cooling the desired substance was obtained in a crystallised condition. After recrystallisation from glacial acetic acid, nitromethoxystilbene formed beautiful, orange needles, melting at 162° (uncorr.):

0.1035 gave 0.2686 CO₂ and 0.0455 H₂O. C=70.8; H=4.8.

C₁₅H₁₃O₃N requires C=70.6; H=5.0 per cent.

The substance dissolves fairly readily in benzene, sparingly in alcohol; it is reddened by concentrated sulphuric acid. Attempts at isolating oxonium salts were unsuccessful.

α-p-Nitrophenyl-p-methoxycinnamic Acid,

—Eighteen grams of nitrophenylacetic acid were converted into the sodium salt, and heated for eight hours with 13.5 grams of anisaldehyde and 50 grams of acetic anhydride. The excess of acetic anhydride was destroyed by dilute alcohol; the product obtained by pouring into water was tarry at first, but solidified on keeping. The acid was purified by solution in sodium carbonate, reprecipitation by hydrochloric acid, and crystallisation from alcohol; it forms an orange, crystalline powder, melting at 231° (uncorr.):

0.1188 gave 0.2849 CO₂ and 0.0493 H₂O. C=64.5; H=4.6.

C₁₆H₁₃O₅N requires C=64.2; H=4.3 per cent.

Absorption Spectra.

On reference to the two figures it will be seen that there is in each case a well marked absorption band. Taking the heads of the absorption bands, it is noticeable that the introduction of the hydroxyl group into stilbene lowers the oscillation frequency by about 70 units, the nitro-group by about 500 units. Fig. 1 shows that the oscillation frequencies of hydroxy- and methoxy-stilbene are fairly close together, but on converting the former into the sodium salt the oscillation frequency is reduced between 200 and 300 units. In Fig. 2 stilbene is compared with nitrostilbene and derivatives of the latter substance. Again it will be noticed that the heads of the absorption bands of the hydroxy- and methoxy-derivatives lie not very far from that of the parent nitrostilbene, but that where the hydroxy-compound is converted into the sodium salt a shift of between 500 and 600 units occurs. The differences in oscillation frequency are even more marked when considered in the following manner: The effect of introducing a nitro-group into stilbene is to shift the head of the band by about 500 units; com-

paring hydroxystilbene and its nitro-derivative, the shift is between 600 and 700 units; but between the heads of the bands in the cases of the sodium salts of hydroxystilbene and its nitro-derivative there

FIG. 1.
Oscillation frequencies.

- I. *Stilbene in alcoholic solution.*
- II. *Nitro-stilbene in alcoholic solution.*
- III. *Hydroxystilbene in alcoholic solution.*
- IV. *" " sodium hydroxide.*
- V. *Methoxystilbene in alcoholic solution.*

is a difference of between 900 and 1000 units. The changes are similar to those observed in the azo-series, and it may be that the difference in behaviour is accounted for by the sodium salts of

hydroxystilbene and nitrohydroxystilbene having different structures, phenolic in the former case, quinonoid in the latter. Whilst

FIG. 2.

Oscillation frequencies.

- I. *Stilbene.*
- II. *Nitrostilbene.*
- III. *Nitrohydroxystilbene in alcoholic solution.*
- IV. *" " sodium hydroxide.*
- V. *Nitromethoxystilbene.*

it may be readily admitted that the structure of a substance containing replaceable hydrogen is the same as that of an alkyl derivative if the two compounds give practically identical absorption

**Hard Copy of Page 611 Missing
But Photocopy is Available**