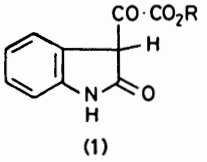
The Purple Pigments produced by Acetylation of 2-(2-Oxoindolin-3-yl)-glyoxylates in the Presence of Pyridine. Some New Evidence

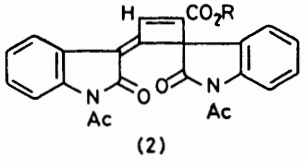
By **James A. Ballantine**, Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP

As a result of the analysis of ^{13}C n.m.r. spectra, a new structure (7) is preferred for the purple pigments obtained by the reactions of 2-(2-oxoindolin-3-yl)glyoxylates with acetic anhydride in the presence of pyridine. A mechanistic rationalisation of the formation of the pigments and their unusual rearrangement on oxidation with chromic acid are discussed.

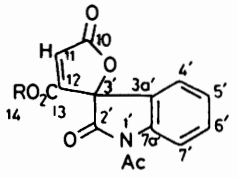
Our recent publication [1] on the structures of the purple pigments obtained by acetylation of 2-(2-oxoindolin-3-yl)glyoxylates (1) suggested a possible structure (2)



(1)



(2)



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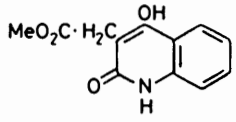

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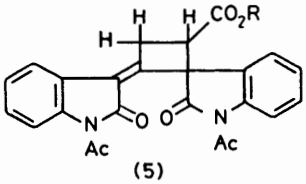

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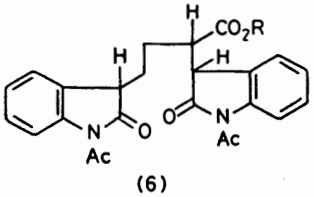


(6)

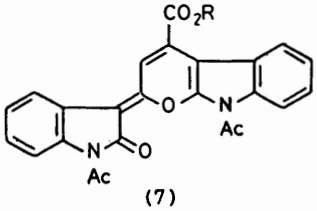
for the pigments. The major degradative evidence leading to this spiro-cyclobutene structure was obtained by chromic acid oxidation of the pigment, when the spiro-lactone (3) was obtained, which could be converted to the hydroxyquinolone (4) after treatment with sodium methoxide. A second degradation sequence using zinc in acetic acid gave a leuco-compound, which was formulated as (5) and could be further reduced by catalytic hydrogenation to the reduced leuco-compound (6).

Although it has not been possible to obtain ^{13}C n.m.r. spectra on the very insoluble pigments, two close derivatives, the benzyl ester oxidation product (3; R = CH_2Ph) and the methyl ester leuco-compound, were soluble enough to obtain satisfactory ^{13}C spectra. Almost all the carbon atoms in each compound were observed as individual singlets in the ^1H noise-decoupled spectra, overlapping resonances only being observed with some of the aromatic methine carbon atoms. The precise assignments of all the carbon chemical shifts in these complex compounds were not possible, but by the use of off-resonance measurements and by the examination of model compounds, many specific assignments were possible. The results are tabulated in the Table.

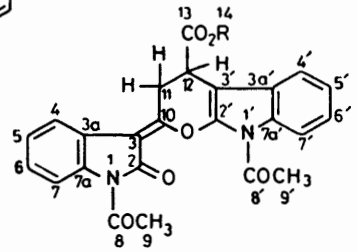
It was clear from this n.m.r. evidence that although the structure of the benzyl ester oxidation product would seem to be correctly formulated as (3; R = CH_2Ph), the ^{13}C n.m.r. spectrum of the methyl ester leuco-compound could not support the proposed structure (5). In particular, the spiro carbon resonance, which was assigned to a quaternary carbon at 85.3 p.p.m. in the oxidation product (3) and should have appeared lower for the leuco-compound, was absent. The corresponding saturated carbon atom in 1-acetyl-2-oxoindole resonates at 36.5 p.p.m. and the spiro carbon atom of the spiro-oxindole alkaloid gelsemine at 54.3 p.p.m.,[2a] so that the expected value for the 3′ carbon atom in structure (5) might be in the range 60—70 p.p.m.

Accordingly, an alternative structure (7) for the pigments is proposed in accord with the ^{13}C n.m.r. spectrum of the leuco-compound which is formulated as (8).

The relative position of carbon atom 3′ in the leuco-compound spectrum at 94.4 p.p.m., when compared with that of the corresponding carbon atom in 3-methylindole (110.9 p.p.m.),[2b] can be accounted for by the increased shielding of the neighbouring vinylic oxygen atom present in structure (8). This effect can be observed by



(7)



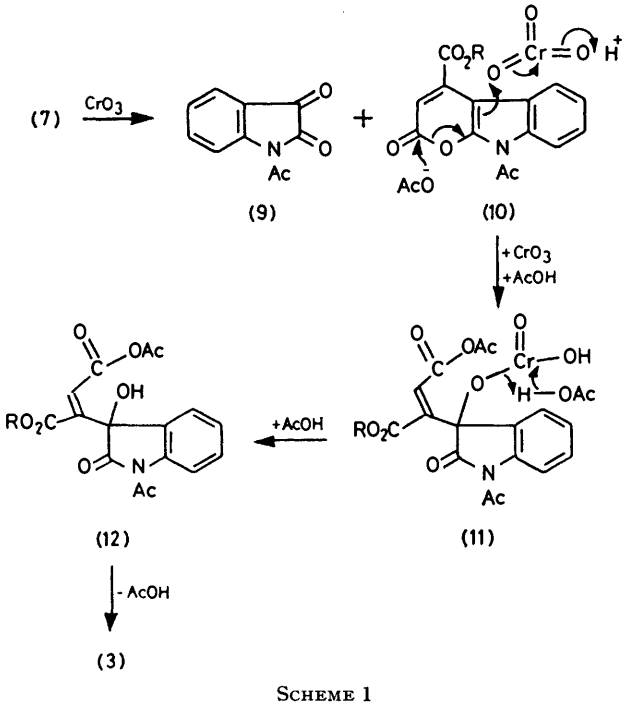
(8)

^{13}C N.m.r. chemical shifts * and assignments †

Methyl leuco-compound (8; R = Me)		Benzyl ester oxidation product (3; R = CH_2Ph)		1-Acetyl-2,3-dioxoindole		1-Acetyl-2-oxoindole		1-Acetoxy-(1-acetyl-2-oxoindolin-3-ylidene)-ethane (14; R = Ac)	
p.p.m.	carbon	p.p.m.	carbon	p.p.m.	carbon	p.p.m.	carbon	p.p.m	carbon
171.4 170.9 168.4 167.7 160.9	2,8,8′, 10,13′	169.9 169.7 168.8 158.9	2′,8′, 10,13	180.1 169.7 157.9	3,2 8	175.2 170.7	3,8	170.8 167.8 166.9 161.7	2,8, 10,10a
143.4 137.2 131.7 125.7 121.6	2′,7a, 7a′,3a, 3a′	153.4 141.6 133.4 121.1	12 7a′,15, 3a′	148.6 11912	7a 3a	141.4 123.9	7a 3a	137.8 121.6	7a 3a
128.9 124.8 124.4(2) 123.7 118.1 116.2 115.9	4,5,6, 7,4′,5′, 6′,7′	132.3 129.1 128.9(2) 128.5(3) 125.9 123.0 117.7	4′,5′,6′, 7′,16,17, 18,19,20, 11	138.9 126.1 125.2 118.2	4,5, 6,7	128.1 124.9 123.9 116.6	4,5, 6,7	129.1 124.8 122.8 116.3	4,5, 6,7
109.9 94.5 52.5 33.9	3 3′ 14 12	85.3 68.6	3′ 14			36.5	3	115.4	3
27.0 26.8	9,9′	26.1	9′	26.3	9	26.5	9	26.9 21.3 19.0	9 11 10b
24.9	11								

* Downfield from tetramethylsilane. * For carbon numbering system refer to structures (8) and (3).

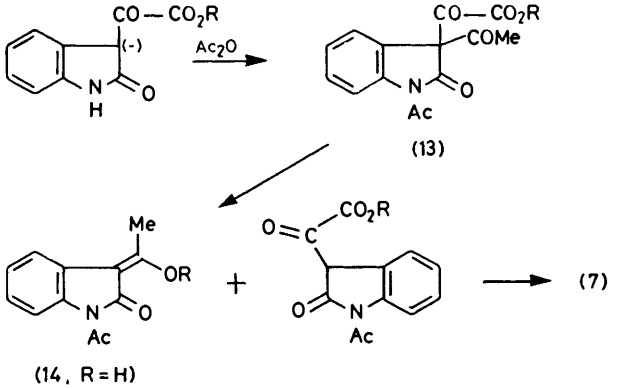
comparing the chemical shift of the methylene atom in 3-chloropropene (118 p.p.m.) [2c] with that of the corresponding methylene atom in acetoxyethene (96.8 p.p.m.).[2d]



SCHEME 1

The proposed structure (7) for the pigments can readily account for the published infrared spectrum and gives a more satisfactory rationalisation of the observed visible spectrum than the original structure (2). Also, the dihydropyran structure (8) for the leuco-compound can account for the AMX system observed in the ^1H n.m.r. spectrum and the reason for the different chemical shifts of the geminal protons (at τ 5.16 and 6.88) can be explained by examination of a model of (8). One of the two geminal protons is selectively affected by the neighbouring 1-acetyl-2-oxoindolin-3-ylidene system in the obvious half-chair conformation of the dihydropyran ring.

The reductive degradation of the pigment can readily be understood on the basis of structure (7), but the oxidative degradation must involve a complex rearrangement. A mechanistic rationalisation of this process is formulated in Scheme 1. Oxidative cleavage



SCHEME 2

of the exocyclic double bond would furnish 1-acetyl-2,3-dioxindole (**9**) and an indolopyrone (**10**) which could be ring-opened at the sensitive 3-position with chromic and acetic acids. (Many indoles and carbazoles can add even molecular oxygen at their sensitive 3-position).[3] The ring-opened chromate ester (**11**) could solvolyse to give the alcohol (**12**) which could then cyclise to give the spiro-lactone product (**3**).

The mode of formation of structure (**7**) for the pigments can easily be rationalised in terms of Scheme **2**. Acylation of the carbanion could give the β-triketone (**13**) which can then eliminate pyruvate to yield the enol (**14**), which has been found as a secondary product in the reaction mixture. Coupling of (**14**) with the *N*-acetylated glyoxylate would yield the proposed structure (**7**).

EXPERIMENTAL

^{13}C N.m.r. spectra were measured for solution in deuteriochloroform using a Varian XL-100 instrument.

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[2] L. F. Johnson and W. C. Jankowski, 'Carbon-13 N.M.R. Spectra,' Wiley, New York, 1972 (*a*) spectrum no. 485; (*b*) spectrum no. 341; (*c*) spectrum no. 22; (*d*) spectrum no. 61.

[3] R. J. Sundberg, 'The Chemistry of Indoles,' Academic Press, New York, 1970, pp. 282—295.