consequently, the results must be treated with some reserve. It may be noted that the analysis for the basic amino acids by Corfield, Howitt and Robson (Table I, footnote *z*) used the chromatographic technique on 15-cm. columns which we have employed; the results are in good agreement. The work of Roche, Michel and Bozzi-Tichadou (Table I, footnote *al*) suggests that the composition of the silk fibroin of *Bombyx mori* may depend upon the exact geographical source of the silk; perhaps some variations in the results of the literature may be attributed to this cause.

Literature references to amino acid analyses of TSF are fragmentary but would indicate a difference between BSF and TSF.

NOTE ADDED IN PROOF.—Since this manuscript was submitted, a translation of the paper by Tsiutsevich and Botvinik (Table I, footnote *ao*) has been obtained. They comment also upon the reversal in the ratio of glycine to alanine in the two fibroins. Attention should be called to a recent paper of F. Lucas, J. T. B. Shaw and S. G. Smith (*Shirley Institute Memoirs*, **28**, 77 (1955)), which lists partial analyses of fibroins from *Bombyx mori* silk, from several Tussah silks, and from three *Anaphe* silks.

Acknowledgments.—We wish to express our thanks to Professor S. Mizushima for supplying the sample of Tussah silk and to Dr. C. H. W. Hirs for the details of the separation of tyrosine on Dowex 2 prior to publication. This investigation was supported in part by a contract between the Quartermaster Corps, U. S. Army and the California Institute of Technology.

PASADENA 4, CALIFORNIA

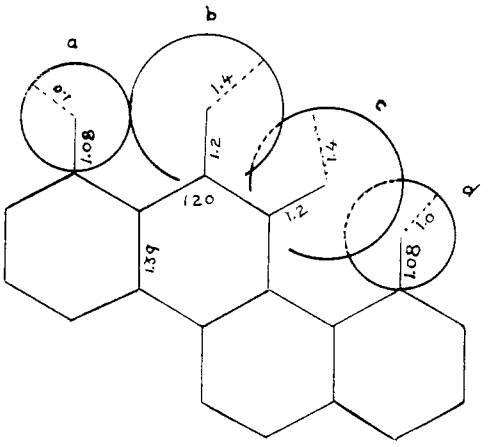
NOTES

Studies on Chrysenoxazoles

BY WILLIAM IBRAHIM AWAD AND ABDEL REHIM ABDEL RAOUF

RECEIVED MARCH 1, 1955

It was found recently[1] that chrysenequinone (I) reacts with aldehydes and ammonium acetate in acetic acid to give chrysenoxazoles and not imidazoles as expected from the general procedure for the preparation of phenanthrimidazoles[2] and have concluded that, in contrast to phenanthraquinone, one carbonyl group of chrysenequinone is more active than the other.

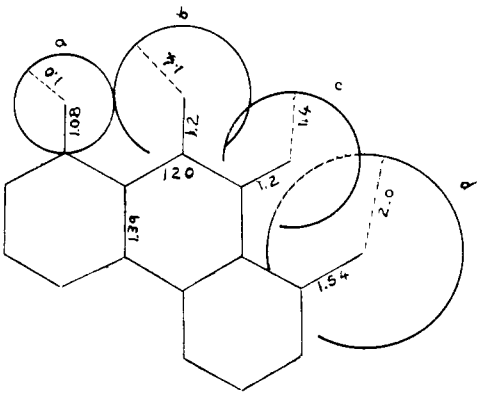


I, a and d = H
b and c = carbonyl group

In continuing this investigation, we have allowed some amines ($R-CH_2-NH_2$) to react with chrysenequinone under pressure. The products obtained were even under these conditions the corresponding oxazoles (II) and not the imidazoles.[3]

2-Methylchrysenoxazole also has been prepared by the action of diazoethane on chrysenequinonimine in a similar manner to the action of diazomethane on chrysenequinonimine.[1]

Another attempt to prepare chrysenimidazoles through the interaction of the diimine acetate and aldehydes was unsuccessful since chrysenequinone when allowed to react with ammonium acetate in acetic acid did not yield the diimine acetate[4] as expected. A pale yellow compound was obtained which we believe to be chrysenequinonimine anhydride (III), since it proved to be identical with the



II, a = H
b, c = carbonyl group
d = methyl group

—, bond distances; ------ van der Waals radii.

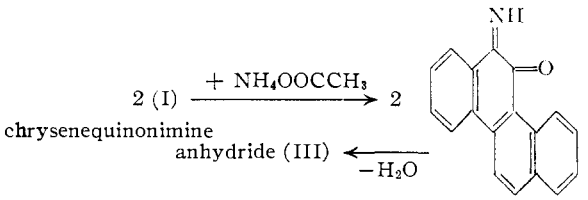
(1) W. I. Awad and A. R. A. Raouf, THIS JOURNAL, **77**, 1013 (1955).

(2) E. A. Steck and A. R. Day, *ibid.*, **65**, 452 (1943).

(3) Compare the reactions of phenanthraquinone and retenequinone with amines under pressure by G. M. Jaffe and A. R. Day, *J. Org. Chem.*, **8**, 43 (1943).

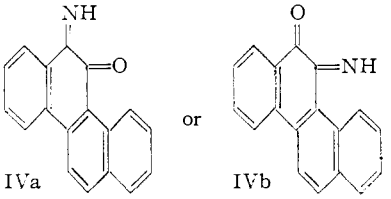
(4) For the preparation of phenanthraquinone diimine acetate and its interaction with aldehydes to give phenanthrimidazoles, compare ref. 2.

compound obtained by the dehydration of chrysenequinonemonoimine with acetic anhydride.[5]



This compound was obtained also, according to a German Patent[6] by allowing ammonia to react with chrysenequinone in boiling nitrobenzene, but no constitution was assigned to it.

It is clear from the above reactions that in contrast to phenanthraquinone, chrysenequinone has one carbonyl group more active than the other. On drawing the chrysenequinone molecule (I) using the known bond distances and van der Waals radii,[7] one can conclude that the carbonyl group (c) near the naphthalene nucleus is hindered more sterically than the other carbonyl group (b). Thus it would appear that chrysenequinonimine is represented best as IVa rather than IVb, since it could be prepared by the action of alcoholic ammonia on the quinone at room temperature.[1]



The oxazole is most probably derived from this structure.[1]

Similarly, retenequinone (1-methyl-7-isopropylphenanthraquinone (II)) has one carbonyl group (c) more sterically hindered by the proximity of the methyl group (d), than the other carbonyl group (b). Schönberg and Awad[8,9] have discussed the uncertainty of the structure of retenequinonimine, but in our opinion it is the carbonyl group (b) that is converted to —C=NH grouping, especially it is obtained by the action of alcoholic ammonia on retenequinone at room temperature.[10]

Retenoxazoles most probably have the corresponding structure and not that mentioned in a previous paper.[9] As an experimental proof for the difference in activity of the two carbonyl groups of retenequinone, Jaffe and Day[3] have found that this quinone when allowed to react with amines ($RCH_2{\cdot}NH_2$) under pressure yielded only oxazoles and not imidazoles.

Steck and Day[2] found that retenequinone when heated with ammonium acetate in glacial acetic acid, yielded a compound which was not the diimine but in their opinion may be aminoretenol. However, by carrying out this reaction in the presence of aldehydes they obtained reteniimidazoles (mixed with retenoxazoles), although they have failed to isolate the diimine as an intermediate.

In our opinion, their compound (the aminoretenol) is more likely to be retenequinonimine anhydride in analogy with the corresponding compound obtained from chrysenequinone. However, this problem is still under investigation.

(5) For the preparation of phenanthraquinonimine anhydride by the dehydration of the corresponding imine compare A. Schönberg and B. Rosenthal, *Ber.*, **54**, 1789 (1921).

(6) German Patent 659,593; *Cent. Blatt.*, **II**, 1491 (1938).

(7) Linus Pauling, "The Nature of the Chemical Bond," 2nd. Ed. (1950), Geoffrey Cumberlege, Oxford University Press, London.

(8) A. Schönberg and W. I. Awad, *J. Chem. Soc.*, 651 (1947).

(9) *Ibid.*, 72 (1950).

(10) von Eugen Bamberger and S. C. Hooker, *Ann.*, **229**, 121 (1885).

Experimental[11]

Preparation of 2-Alkyl- and 2-Arylchrysenoxazoles from Chrysenequinone and the Corresponding Amine, under Pressure. (a) **2-Methylchrysenoxazole.**—Five-tenths gram of chrysenequinone and 10 ml. of 25% aqueous ethylamine, in 15 ml. of ethyl alcohol, was heated at 100° in a sealed tube for 6 hours. The product obtained by cooling was recrystallized from ethyl alcohol as pale yellow needles, m.p. 167°, undepressed on admixture with the product of diazoethane on chrysenequinonimine; yield 0.2 g. It gave no color with concentrated sulfuric acid.

Anal. Calcd. for $C_{20}H_{13}ON$: C, 84.8; H, 4.6; N, 4.9. Found: C, 83.9; H, 4.64; N, 4.7.

(b) **2-Ethylchrysenoxazole.**—Five-tenths gram of chrysenequinone, and few drops of *n*-propylamine, in 20 ml. of benzene were heated at 100° in a sealed tube for 6 hours. The product came down after concentration and cooling, and was recrystallized from methyl alcohol–benzene mixture to give pale yellow crystals, m.p. 156°, yield 0.3 g. It gave no color with concentrated sulfuric acid. The product was proved to be 2-ethylchrysenoxazole by m.p. and mixed m.p. determinations.[1]

Anal. Calcd. for $C_{21}H_{15}ON$: C, 84.8; H, 5.1; N, 4.7. Found: C, 84.9; H, 5.3; N, 4.8.

(c) **2-*n*-Propylchrysenoxazole.**—Five-tenths gram of chrysenequinone and a few drops *n*-butylamine in 20 ml. of benzene were heated at 100° in a sealed tube for 6 hours. The benzene was evaporated and the residue was recrystallized from methyl alcohol to give pale yellow needles, m.p. 116–117° brown melt, yield 0.4 g. It gave blue-green color with concentrated sulfuric acid, then the color faded. The product was proved to be 2-*n*-propylchrysenoxazole by m.p. and mixed m.p. determinations.[1]

Anal. Calcd. for $C_{22}H_{17}ON$: C, 84.9; H, 5.5; N, 4.5. Found: C, 85.2; H, 5.6; N, 4.6.

(d) **2-Phenylchrysenoxazole.**—Five-tenths gram of chrysenequinone, and few drops of benzylamine, in 10 ml. of benzene were heated at 120° in a sealed tube for 8 hours. The product obtained on cooling was recrystallized from xylene to give colorless fluffy crystals, m.p. 268–269°, yield 0.3 g. It gave a yellow color with concentrated sulfuric acid. The product was proved to be 2-phenylchrysenoxazole by m.p. and mixed m.p. determinations.[1]

Preparation of Chrysenequinonimine Anhydride (III).—One gram of chrysenequinonimine and 15 ml. of acetic anhydride was heated for 20 minutes on a steam-bath and the product filtered while hot. It was recrystallized from nitrobenzene to give yellow crystals, m.p. 320°, yield 50%. The m.p. was undepressed on admixture with the product of the action of ammonia on quinone in boiling nitrobenzene.[5] It gave no color with concentrated sulfuric acid.

Anal. Calcd. for $C_{36}H_{20}ON_2$: N, 5.7. Found: N, 5.8.

Action of Ammonium Acetate and Glacial Acetic Acid on Chrysenequinone.—When 2 g. of chrysenequinone, 16 g. of ammonium acetate and 25 ml. of glacial acetic acid were refluxed for 1 hour, a deposit began to separate in 10 minutes. The product was filtered, recrystallized from benzene, toluene or xylene to give yellow crystals, m.p. 320°, undepressed on admixture with the product from acetic anhydride and chrysenequinonimine; yield 1.8 g. It gave no color with concentrated sulfuric acid.

Anal. Calcd. for $C_{36}H_{20}ON_2$: C, 87.1; H, 4.0; N, 5.7. Found: C, 87.4; H, 4.2; N, 5.8.

Action of Diazoethane[12] on Chrysenequinonimine.—Two-tenths gram of the imine was suspended in ether, cooled in an ice-bath, treated with an excess of ethereal diazoethane

(11) Microanalyses were carried out by Alfred Bernhardt, Germany. Melting points are not corrected.

(12) E. A. Werner, *J. Chem. Soc.*, **115**, 1093 (1919).

solution and left for 6 hours. The ether then was evaporated and the residue recrystallized from methyl alcohol to give pale yellow needles, m.p. 167°, yield 0.1 g. It gave no color with concentrated sulfuric acid. This product was proved to be 2-methylchrysenoxazole by m.p. and mixed m.p. determinations.[13]

Anal. Calcd. for $C_{20}H_{13}ON$: C, 84.8; H, 4.6; N, 4.9. Found: C, 84.8; H, 4.5; N, 4.7.

(13) In ref. 9 the m.p. of 2-methylchrysenoxazole is stated as 223°.

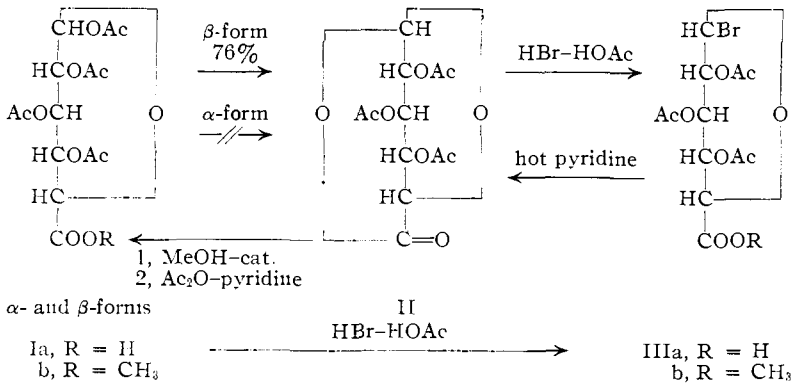
DEPARTMENT OF CHEMISTRY
AIN SHAMS UNIVERSITY
ABBASSIA, CAIRO, EGYPT

Tri-*O*-acetyl-β-D-glucopyranurono-6,1-lactone

BY E. M. FRY

RECEIVED FEBRUARY 9, 1955

The synthesis of tri-*O*-acetyl-β-D-glucopyranurono-6,1-lactone (II) was undertaken in order to see whether or not this compound is a suitable intermediate for the preparation of alkyl β-D-glucopyranosiduronic acids. The approach was made



attractive by the work of Lemieux who showed that the carbon-1 β-acetoxy group of an acetylated glucose is subject to displacement by an alkoxyl group in the presence of stannic chloride. Thus, 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose was converted into tri-*O*-acetyl-1,6-anhydro-β-D-glucopyranose in 36% yield,[1b] and penta-*O*-acetyl-β-D-glucopyranose into methyl tetra-*O*-acetyl-β-D-glucopyranoside in 50–60% yield.[1c] The configuration of the α-anomers makes them unsuitable for this type of displacement and an adequate discussion and review is to be found in Lemieux' paper.[1a]

The acetylation of sodium glucuronate in the presence of *p*-toluenesulfonic acid gave two anomeric tetraacetylglucuronic acids Ia, which were identified by conversion into the known methyl esters Ib.[2a] As expected, the α-form in benzene solution in the presence of stannic chloride was recovered for the most part unchanged, whereas the β-acid yielded a crystalline compound insoluble in sodium carbonate. The elemental analysis is that required by tri-*O*-acetyl-β-D-glucopyranurono-6,1-lactone (II) and the yield on this basis was 76%. Its structure follows from ring-opening with hydrobromic acid to give (tri-*O*-acetyl-α-D-glucopyranosyl bromide)-uronic acid (IIIa) identical with the compound obtained from both α- and β-forms of tetra-*O*-acetyl-D-glucopyranuronic acid (Ia). Esterification with diazomethane gave methyl (tri-*O*-acetyl-α-D-glucopyranosyl bromide)-uronate (IIIb), isolated in two crystalline modifications, one of which has been described.[2b] When the bromide IIIa was heated in pyridine it was reconverted in small yield to the lactone. The β-configuration at carbon-1 is the only one structurally possible in a lactone derived from a D-glucopyranuronic acid and its formation is consistent with previous experience in related reactions.[1a]

The lactone reacts normally with excess methanol in the presence of catalysts such as pyridine, pyridine-*p*-toluenesulfonic acid salt, and silver carbonate to give oily methyl 2,3,4-tri-*O*-acetylglucopyranuronate, identified by conversion to methyl tetra-*O*-acetyl-β-D-glucopyranuronate (Ib).

It was expected that both the lactone II and the β-form of the methyl ester Ib, would react with methanol in benzene in the presence of stannic chloride to give methyl tri-*O*-acetyl-β-D-glucopyranosiduronic acidand its methyl ester, respectively, but in no case could any of the desired material be isolated from the oily product. That the carbonyl group is favorably situated for interaction with carbon-1 is demonstrated by the ease with which it displaces an acetoxy group in this position, and it is possible that the failure of these compounds to react in the expected way with methanol is in some way related to the influence of the carbonyl group.

Acknowledgment.—The author is grateful for the interest and help of Dr. Erich Mosettig and Dr. Robert K. Ness. Microanalyses were made by the Institutes service laboratory under the direction of Dr. William C. Alford.

Experimental

α- and β-Anomers of Tetra-*O*-acetyl-D-glucopyranuronic Acids (Ia).—Fifty grams of glucuronolactone was dissolved in 175 ml. of water and 25 g. of sodium bicarbonate added at room temperature. Carbon dioxide was evolved and in 5 hours the solid dissolved completely. After standing overnight water was removed under reduced pressure at 40°. The residual oil was triturated with ethanol in which it is not soluble. After removing the alcohol under reduced pressure the yellow sodium salt was obtained crystalline. It weighed 66.8 g.[3] Sixty-five grams of *p*-toluenesulfonic acid hydrate was dissolved in 230 ml. of acetic anhydride and the solution chilled in acetone–Dry Ice to 0° and held at this temperature. The powdered sodium salt was added fairly rapidly with mechanical stirring. It dissolved for the most part in 30 minutes at which time sodium *p*-toluenesulfonate began to separate. After a time (not recorded but approximately one hour) the cold mixture was diluted with two volumes of ether and shaken with an aqueous solution of 7 g. of sodium acetate to remove excess *p*-toluenesulfonic acid (separation into two phases occurs only with relatively large amount of water). The aqueous phase was extracted with chloroform and the organic solutions joined and the solvents

(1) (a) R. U. Lemieux, *Can. J. Chem.*, **29**, 1079 (1951); R. U. Lemieux, *Advances in Carbohydrate Chem.*, **9**, 1 (1954); (b) R. U. Lemieux and C. Brice, *Can. J. Chem.*, **30**, 295 (1952); (c) R. U. Lemieux and W. P. Shyluk, *ibid.*, **31**, 528 (1953).

(2) (a) W. F. Goebel and F. H. Babers, *J. Biol. Chem.*, **106**, 63 (1934); (b) **111**, 347 (1935).

(3) An improved method for making this salt has been published by W. Hach and D. G. Benjamin, THIS JOURNAL, **76**, 917 (1954).