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REACTIONS OF α-CHLOROISATIN (2-CHLOROINDOLENINONE) WITH METHANETHIOL AND 1,2-ETHANEDITHIOL.

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In studies on precursors to Tyrian purple from the hypobranchial glands of gastropod molluscs of the family *Muricidae*, Baker and Sutherland[1] found that reaction of the ether extract of the freshly excised glands of *Dicathais orbita* with excess diazomethane yielded spiro[6-bromo-2-methylthioindoleninone-3,2'-oxirane] (I) and 7-bromo-2-methylthio-3-methoxyquinoline (II), it being proposed[2] that this reaction could proceed through an indoleninone intermediate of type (III) which is a partially dehydrogenated product of the indoxyl (IV) produced by enzymic hydrolysis of the absolute precursor (V) to the purple compound 6,6'-dibromoindigotin.

The proposed intermediate (III) is a derivative of the previously unreported 2-methylthioindoleninone (VI).

Reaction of isatin with phosphorous pentachloride gave 2-chloroindoleninone (VII)[5] [80% yield] which reacted at room temperature with anhydrous methanethiol and with 1,2-ethanedithiol to give the previously unreported 2,2-dimethylthio-3-indolinone (VIII) [53% yield][3] and spiro[3-indolinone-2,1'-2',5'-dithiocyclopentane] (IX) [74% yield] respectively. The position isomer of (IX), spiro [2-indolinone-3,1'-2',3'-dithiocyclopentane] (X) has been previously reported[4]. In the presence of water and methanethiol in benzene, 2-chloroindoleninone (VII) gave 3,3-dimethylthio-2-indolinone (XI) [16% yield].

Physical measurements:

(VI) C_9H_7NOS: red needles m.p. 133-134°: M^{+}. 177: p.m.r. [CCl_4, δ] s, 2.61 (3H), $-SCH_3$: m. 7.3 (4H) aromatic.

(VIII) $C_{10}H_{11}NOS_2$: yellow needles m.p. 81-83° (decomp.): M^{+} 225 (loses CH_3SH to m/e 177): p.m.r. [CCl_4, δ] s, 2.19 (6H), $-SCH_3$: br. s. 5.36 (1H) -NH-: m. 7.2 (4H) aromatic.

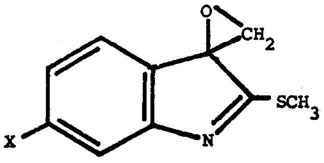
(IX) $C_{10}H_9NOS_2$: yellow prisms m.p. 139° (decomp.): M^{+} 223: p.m.r. [$CDCl_3$, δ] s, 3.68 (4H),

$-S-CH_2-CH_2-S$: br. s. 4.5 (1H) -NH-: m. 7.2 (4H) aromatic.

(XI) $C_{10}H_{11}NOS_2$: colourless needles m.p. 159°: M^+ 225: p.m.r. [$CDCl_3$, δ] s 2.19 (6H) $-SCH_3$: m. 7.2 (4H) aromatic: br. s. 9.53 (1H) -NH- (amide).

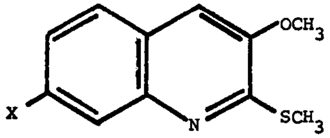
Whereas the spirodithio compound (IX) is stable, the dimethylthio compound (VIII) partially decomposes at room temperature to give an equilibrium mixture containing (VIII) and 2-methylthioindoleninone (VI), and when refluxed in toluene (VIII) is converted to (VI) [73% yield].

An ether solution of (VI) on reaction with excess diazomethane gave spiro[2-methylthioindolenine-3,2'-oxirane] (XII) [25% yield] and 2-methylthio-3-methoxyquinoline (XIII) [40% yield].



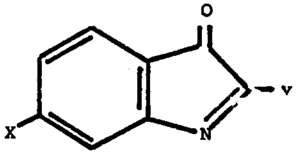
I, X = -Br

XII, X = -H



II, X = -Br

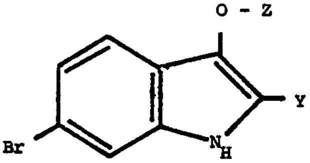
XIII, X = -H



III, X = -Br, Y = $-SCH_3$

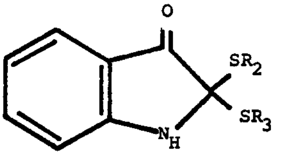
VI, X = -H, Y = $-SCH_3$

VII, X = -H, Y = -Cl



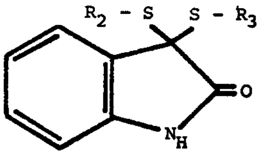
IV, Y = $-SCH_3$, Z = -H

V, Y = $-SCH_3$, Z = $-OSO_2ONa$



VIII, $R_2 = R_3 = -CH_3$

IX, $R_2R_3 = -CH_2-CH_2-$



X, $R_2R_3 = -CH_2-CH_2-$

XI, $R_2 = R_3 = -CH_3$

REFERENCES

1. J.T. Baker and M.D. Sutherland, Tetrahedron Letters, 1968, 43 [structure III corrected 1968, No. 26].
2. J.T. Baker, Ph.D. Thesis, University of Queensland, 1967.
3. All previously unreported compounds described in this paper give satisfactory elemental analyses; i.r., n.m.r. and mass spectra are consistent with the proposed structures.
4. E. Wenkert and N.V. Bringi, J. Amer. Chem. Soc., 80, 5575 (1958).
5. A. von Baeyer, Ber., 12, 456 (1879).