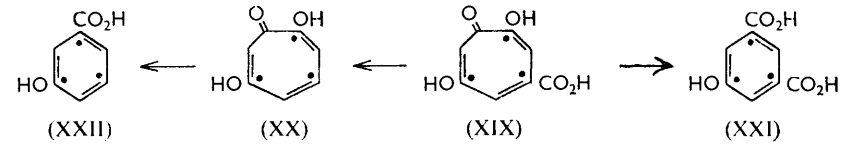
Addendum

By W. Segal.

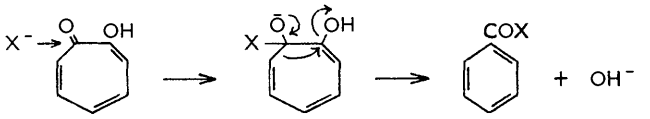
The alkali-rearrangement of the specifically labelled stipitatic acid (XIX) and 4-hydroxytropolone (XX) gives 5-hydroxyisophthalic acid (XXI) and *m*-hydroxybenzoic acid (XXII), respectively, in which the carboxyl carbon atoms are essentially devoid

[29] Tollens, *Ber.*, 1881, **14**, 1950.

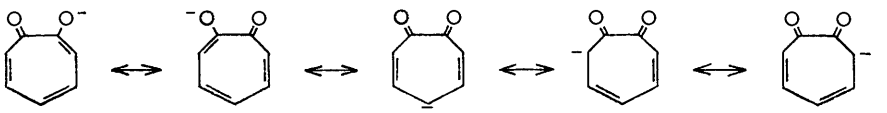
of activity. Johnson [30] explained the alkali- and allied rearrangements of tropolones by the scheme (XXIII), and Doering and Denney [31] substantiated this for [1-^{14}C]halogenotropones, showing that it is the carbonyl-carbon atom which is extruded. The planarity, regularity, and equal lengths of $C_{(1)}$–O and $C_{(2)}$–O bonds [32] of the tropolonate anion (XXIV) reflect its mesomeric nature.



(XXII) (XX) (XIX) (XXI)



(XXIII)



(XXIV)

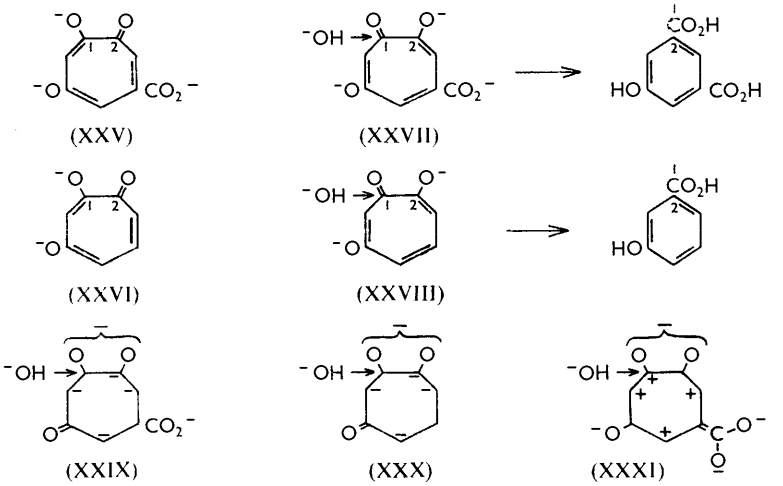
On the assumption that the anions of stipitatic acid and 4-hydroxytropolone exhibit resonance of the α-enolate system as in (XXIV); alkali-isomerization of (XIX) and (XX) would be expected to extrude C-1 and C-2 equally, affording products in which the extruded carbon atom should bear one-sixth of the activity. The absence of activity in these carbons atoms of (XXI) and (XXII) is apparently due to the exclusive attack by hydroxyl ion at C-1, the $C_{(1)}$–O bond possessing significantly higher carbonyl character than the $C_{(2)}$–O bond. This difference in carbonyl character may be explained in terms of charge-crowding inhibition of resonance, and exclusive attack at C-1 may be explained by considering the mesomeric effects of O^- at position 6 in the anions of (XIX) and (XX) and of CO_2^- in the anion of (XIX).

Charge-crowding Inhibition of Resonance.—The dimensions [32] of the regular-planar tropolonate anion, C–C (1·40 Å), $C_{(1)}$–O and $C_{(2)}$–O (1·28 Å), permit estimation of the separation between oxygen atoms at positions 1 and 6 of (XXV) and (XXVI) to be 4·5 Å. The distance between the oxygen at position 2 and the centre of symmetry of the oxygen atoms of the carboxylate group of (XXVII) is calculated to be 6·6 Å. The potential energy of two electrons 4·5 Å apart is 3·2 ev. This energy level is such that, other things being equal, the canonical forms (XXV) and (XXVI) would be expected to be less important than other structures, *e.g.*, (XXVII) and (XXVIII).[33] On this basis the $C_{(1)}$–O bond should have significantly higher carbonyl character than the $C_{(2)}$–O bond, in accord with the exclusive extrusion of C-1 in the isomerization. The anion of decarboxylated stipitatic acid is therefore that of 6-hydroxytropolone rather than the 4-isomer, although the molecule itself is the 4-isomer.

Mesomeric Effects of Substituents.—The 3-, 5-, and 7-positions of tropolone and the tropolonate anion (XXIV) are activated to electrophilic reagents, corresponding to *ortho-*, *meta-*, and *para*-positions of phenol and the phenoxide ion. By a similar process of electromeric displacements from the O^- at position 6 in (XXIX) and (XXX), the electron

[30] Johnson, *J.*, 1954, 1331.
[31] Doering and Denney, *J. Amer. Chem. Soc.*, 1955, **77**, 4619.
[32] Nozoe, " Tropones and Tropolones " in " Non-Benzenoid Aromatic Compounds," ed. D. Ginsburg, Interscience Publ., Inc., New York, 1959.
[33] Personal communication from Professor R. D. Brown.

density is enhanced at C-2 relative to that at C-1. The 1-position is thus activated to nucleophilic attack by hydroxyl ions. The mesomeric effect of the carboxylate group in (XXXI) is to promote nucleophilic attack at position 1 rather than at position 2. These effects reinforce each other, leading to the exclusive extrusion of C-1.



(XXV) (XXVII)

(XXVI) (XXVIII)

(XXIX) (XXX) (XXXI)

One implication of this analysis is that, although the tropolonate anion is symmetrical, there should be a measurable difference in the $C_{(1)}$–O and $C_{(2)}$–O bond lengths of the anions of stipitatic and decarboxylated stipitatic acid.

Part of this work was carried out (by W. S.) during the tenure of an I.C.I. Research Fellowship at the Biochemistry Department, London School of Hygiene and Tropical Medicine, University of London. The authors acknowledge a grant from the Research Committee of the University Grants Committee of New Zealand.

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[*Received, February 21st,* 1963.]