Summary

1. α-Galactose oxime hexaacetate and the hexaacetate and pentaacetate of aldehydo-galactose oxime have been synthesized in pure crystalline form.

2. It is shown that the two oxime hexaacetates above are isomers of the ring–open chain type.

3. The mole of water in the hydrate of aldehydo-galactose oxime pentaacetate has been shown to be held by non-constitutional or secondary valence forces.

4. Galactose oxime has been shown to possess a ring structure of the α-type.

5. The acetylated aldehydo-galactose oximes revert to the ring form on alkaline de-acetylation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A POTENTIOMETRIC STUDY OF SCHOLL'S ANTHROXYL RADICALS

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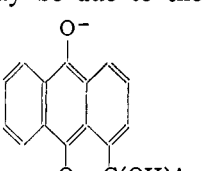
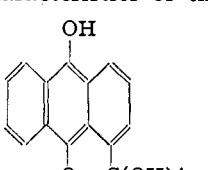
It is generally agreed that the primary oxidation products of all of the monatomic phenols are radicals having univalent oxygen atoms ("oxyls"). The radicals ordinarily are too unstable to have any but a transitory existence, for the free valence shifts from oxygen to carbon and the carbyl radical undergoes various secondary changes. In chlorophenanthrol Goldschmidt and Steigerwald[1] found a compound in which, probably because of the blocking of the positions ortho and para to the oxygen atom, this wandering of the free valence does not occur. Their phenanthroxyls, however, were not completely stable, but associated to form dimolecular peroxides. It remained for Scholl to discover a type of radical which does not manifest even this second kind of instability.[2] That his blue-violet aryl-hydroxyl-*peri*-hydrofurano-anthroxyls of the type of I are strictly monomeric may be due to the spatial characteristics of the anthracene



I



II

[1] Goldschmidt and Steigerwald, *Ann.*, **438**, 202 (1924).

[2] Scholl, *Ber.*, **64**, 1158 (1931).

molecule. Whatever the reason may be, it remains a fact that these remarkable compounds are as stable in the presence of aqueous solvents as many of the quinones, and it is a matter of considerable interest to apply to these compounds the potentiometric methods which have been so fruitful in the study of the oxidation products of the diatomic phenols.

It has been found that an anthroxyl radical in combination with its immediate reduction product (II) forms a reversible oxidation–reduction system having a characteristic and fairly reproducible normal potential. The system is not completely stable, electrode equilibrium is rather slow, and the potentials are not as clearly defined as they are in the case of the majority of quinone–hydroquinone systems; but there is no really essential deviation from the usual behavior.

In planning our experiments we hoped to obtain some information regarding the mode of formation of the radical, for on this point Scholl is not clear. The anthroxyl is formed on the reduction of the corresponding α-aroylanthraquinone, from which it differs by one hydrogen atom, and Scholl, in his first paper,[3] written at a time when the structure of the product was not yet established, considered that the radical is produced directly as the result of the addition of a single hydrogen atom to the quinone. In more recent work[4] the free radical has been prepared by heating the aroylanthrahydroquinone in an acidic medium, when it undergoes some still obscure process of disproportionation.

We prepared a solution of the α-aroylanthraquinone in alcoholic hydrochloric acid, reduced it catalytically at room temperature, and titrated the filtered solution electrometrically in an atmosphere of nitrogen with a solution of benzoquinone. When the titration was carried out very shortly after the reduction, there was obtained a curve (the lower curve in Fig. 1) which is clearly that of the anthraquinone–anthrahydroquinone system, for the slope is that of the two-hydrogen type of oxidation ($n = 2$) and the normal potential of 0.178 v. is very close to the value for anthraquinone itself ($E_0 = 0.154$ v.). Like most other quinones, the α-aroylanthraquinone thus adds two hydrogen atoms simultaneously, even on gentle reduction. When a titration was carried out with a portion of the same reduced solution after it had been allowed to stand for some time, or after it had been heated, there were two distinct portions of the titration curve. The first portion, shown as the lower part of the upper curve in Fig. 1, again had a slope corresponding to $n = 2$ and a mid-point potential of 0.178 v., but it was considerably shorter than that obtained with the fresher solution. It is evident that some of the α-aroylanthrahydroquinone present at the time of the first titration had disappeared on standing. The amount so lost is indicated on the chart by the distance, A, between the two end-points.

[3] Scholl, *Ber.*, **54**, 2376 (1921).

[4] Scholl and Hähle, *ibid.*, **56**, 1065 (1923).

The upper portion of the second curve is quite different. The slope corresponds more nearly to that to be expected in an oxidation which involves a single hydrogen atom (n = 1), and the average value of 0.361 v. found for the normal potential is considerably higher than that for the anthraquinone–anthrahydroquinone system. This part of the titration obviously represents the oxidation of the monatomic phenol, II, to the

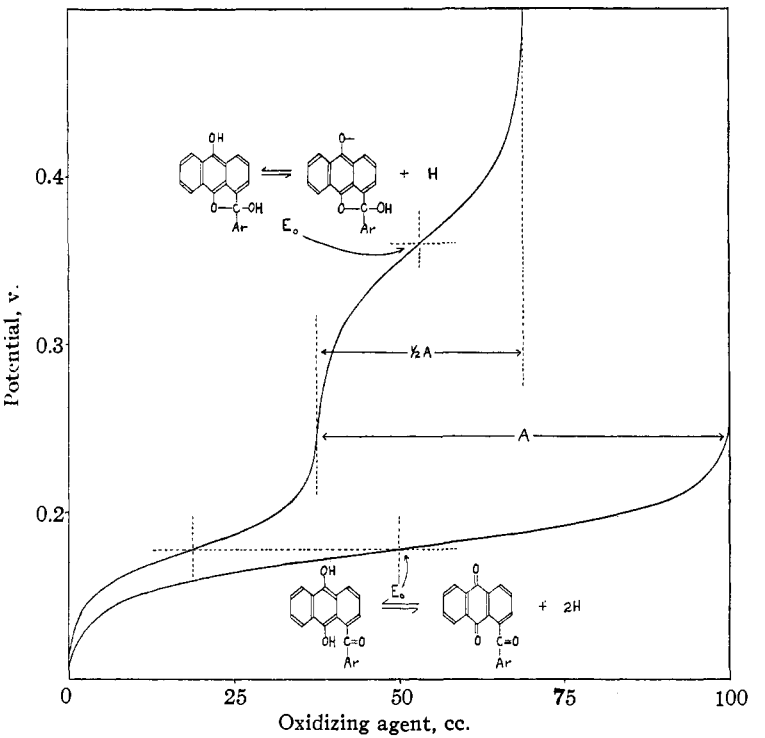
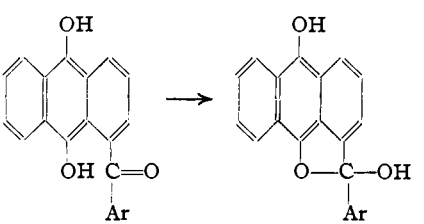


Fig. 1.

anthroxyl radical. It is of significance that the amount of oxidizing solution required for this second part of the titration was found to be approximately half of the quantity, A, which represents the amount of the anthrahydroquinone which disappeared between the first and the second experiment. Since one molecule of the phenol (II) is equivalent to one-



half molecule of the anthrahydroquinone, it is clear that the former substance is produced quantitatively from the latter. The aroylanthrahydroquinone evidently undergoes intramolecular addition of the hydroxyl group to the carbonyl group, the reaction being catalyzed by mineral acids.

If an oxidizing agent is added at this point the phenol is converted into the anthroxyl radical. In the absence of an oxidizing agent, and when heated, the phenol apparently disproportionates to give the radical and an unidentified reduction product.

The compounds included in our study were those obtained from α-benzoyl-, α-[*m*-xyloyl]- and α-[*p*-anisoyl]-anthraquinone. It was found that the potential of the radical system is influenced to only a negligible extent by substitution in the aryl group, and it thus appears unprofitable to pursue this line of investigation further. The interesting nitrogen-containing radicals described by Scholl[5] were also examined, but the potentials were so ill-defined that we can only say that these systems lie in approximately the same potential range as those of the oxyl radicals.

The potentials found for the systems containing the anthroxyl radicals are of course more certain than the values estimated[6] for a number of simply constituted oxyl radicals by an indirect and approximate method, and some comparison of the results is of interest, even though the compounds studied are of such different types that only a very rough comparison is possible. If the reductant (II) of Scholl's radical is regarded as a *p*-alkoxy-anthranol, then it should bear a relationship to anthrahydroquinone similar to that of *p*-methoxyphenol (E_0, 0.984 v.) to hydroquinone (E_0, 0.715 v.). From these figures, the first of which was determined by the indirect method, and from the potential of the anthraquinone–anthrahydroquinone system (E_0, 0.154 v.), Scholl's radical would be expected to form a system having a potential of 0.423 v. This places the system in approximately the right region, the value found being 0.361 v.

Experimental Part

A weighed sample of the aroylanthraquinone was dissolved in the boiling solvent (95% ethyl alcohol, 0.2 *N* in both hydrogen chloride and lithium chloride) and the solution was washed into a hydrogenation bottle, cooled and the total weight of the solution determined. On adding Adams' platinum oxide catalyst and shaking for a few minutes under a slight pressure of hydrogen, the yellow solution became reddish-brown in color. Approximately half of the solution was then forced under hydrogen pressure through a filter and into a titration vessel which had been previously swept free of oxygen by purified nitrogen. The titration vessel was painted black, for the free radical is very sensitive to the light. The vessel was connected to a hydrogen electrode containing some of the same buffer solution, and a titration was performed as rapidly as possible, the end-points of the two curves and the mid-point potentials being estimated graphically. At the end of the titration the weight of the solution taken in the experiment was

[5] Scholl, *Ber.*, **60**, 1236, 1685 (1927); **61**, 968 (1928).

[6] Fieser, THIS JOURNAL, **52**, 5204 (1930).

determined, the weights of the vessel and of the titrating solution being deducted from the total weight. In this way the fraction of the weighed sample which had been used was determined. A titration was then carried out with a second portion of the same original solution, after allowing time for the condensation reaction to take place.

The first titration could be carried out within a few minutes and the potentials were sharply defined and showed only a slight drift. In the second part of the titration the potential after each addition of reagent came to a condition of comparative rest only after several minutes and the final values could not be determined with great accuracy. A typical titration is given in Table I, and the deviations in the values in the last column for the quantity n from the theoretical value of 1.0 will illustrate the general uncertainty of the results which can be obtained in this part of the titration.

TABLE I

TITRATION OF α-[*m*-XYLOYL]-ANTHRAHYDROQUINONE WITH BENZOQUINONE SOLUTION

First curve			Second curve		
Oxid. soln., cc.	E, v.	n	Oxid. soln., cc.	E, v.	n
0.0	0.1162	...	20.0	0.313	...
1.0	.1405	2.0	20.5	.339	...
4.0	.1596	2.0	21.5	.350	1.4
6.0	.1665	1.9	22.5	.359	1.5
8.5	.1737	1.8	23.0	.363	...
10.5	.1792	2.4	24.0	.376	1.0
13.0	.1865	1.9	24.5	.382	1.2
15.0	.1938	1.8	25.0	.391	1.2
17.0	.2042	1.8	25.5	.405	1.2
19.0	.2252	1.8	26.0	.421	1.4
19.5	.2550	1.9	26.5	.520	...
End-point, 19.8 cc.; E_0, 0.178 v.			End-point, 26.2 cc.; E_0, 0.360 v.		

Table II gives a summary of the quantities of reagent consumed in two typical pairs of experiments, all reduced to a common basis. One portion (a) of Solution 1 was titrated fifteen minutes after the completion of the hydrogenation, and it was found to contain both the anthrahydroquinone, which consumed 27.5 cc. of reagent, and the anthranol, which required 5.1 cc. On the assumption that the latter substance requires one-half as much reagent as the former, the total reagent used, in terms of anthrahydroquinone equivalents, is 27.5 + 10.2 = 37.7 cc. This is very close to the amount (last column) calculated from the weight of sample taken and the concentration of the titrating solution. A second check is given by comparing the two titrations, *a* and *b*, on portions of the same

TABLE II

TITRATION OF 0.2 G. OF α-[*m*-XYLOYL]-ANTHRAHYDROQUINONE IN 160 G. OF SOLVENT WITH 0.0157 MOLAR BENZOQUINONE SOLUTION

		Volume of oxidizing solution, cc.					
No.	Time of standing, min.	First curve	Decrease	Second curve	Increase	Equiv. total Found	Calcd.
1a	15	27.5	6.8	5.1	3.3	37.7	37.6
1b	153	20.7		8.4		37.5	37.6
2a	13	28.0	5.8	4.2	3.2	36.4	37.6
2b	132	22.2		7.4		37.0	37.6

solution. After standing for the time specified, Solution 1b contained less of the anthrahydroquinone and more of the anthranol. The change in titer of the latter is approximately half that of the former.

A summary of the average values found for the normal potentials, or the potentials of the half-oxidized solutions against a hydrogen electrode in the same buffer solution at 25°, is given in Table III.

TABLE III

POTENTIALS (E_0) OF THE SYSTEMS FROM α-AROYLANTHRAQUINONES AND THE CORRESPONDING RADICALS

Aryl group	Quinone, v.	Radical, v.
Phenyl-	0.182	0.360
m-Xylyl-	.178	.361
p-Anisyl-	.178	.356

Summary

The free anthroxyl radicals discovered by R. Scholl form, with their reductants, fairly stable oxidation–reduction systems of definite, if not very accurately determinable, potential. In dilute acidic solution the reductant of the radical is formed by the intramolecular condensation of the corresponding α-aroylanthrahydroquinone.

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THE PREPARATION AND GERMICIDAL PROPERTIES OF PARA-HYDROXYPHENYL ALKYL SULFIDES

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Although many investigations of the germicidal properties of alkylated phenolic compounds[1] have been made, the available systematic information demonstrating the influence of alkyl groups not directly attached to the aromatic nucleus has been limited to the recent[1f,2] work on the alkoxyphenols. The present communication describes a study of a series of *p*-hydroxyphenyl *n*-alkyl sulfides, the alkyl group varying from methyl to *n*-hexyl. Since it has been shown by other workers[3] that the hydroxy-

[1] Only some of the more recent articles can be listed here: (a) Johnson and Lane, THIS JOURNAL, **43**, 348 (1921); (b) Dohme, Cox and Miller, *ibid.*, **48**, 1688 (1926); (c) Talbot and Adams, *ibid.*, **49**, 2040 (1927); (d) Klarmann, *ibid.*, **48**, 791, 2358 (1926); (e) Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 280 (1930); (f) Read and Miller, THIS JOURNAL, **54**, 1195 (1932).

[2] Klarmann, Gatyas and Shternov, *ibid.*, **53**, 3397 (1931); **54**, 298, 1204 (1932).

[3] Hilbert and Johnson, *ibid.*, **51**, 1526 (1929); Dunning, Dunning and Drake, *ibid.*, **53**, 3466 (1931); Klarmann, Gates and Shternov, *ibid.*, **54**, 1204 (1932).