[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

A COMPARISON OF HETEROCYCLIC SYSTEMS WITH BENZENE II. REDUCTION POTENTIALS OF QUINONES CONTAINING THE PYRIDINE, IMIDAZOLE, TRIAZOLE AND THIOPHENE RINGS

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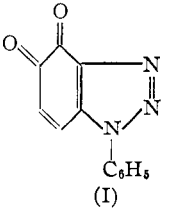
RECEIVED JULY 27, 1927 PUBLISHED OCTOBER 5, 1927

In the first paper of this series[1] a description was given of an experimental method of studying various unsaturated ring systems which consists in comparing, by means of oxidation-reduction potential measurements, the oxidizing power of a compound such as α-naphthoquinone, in which a benzene ring is fused to a quinone grouping, with the oxidizing power of a quinone formed by replacing the benzene ring of α-naphthoquinone by a heterocyclic nucleus. The relative extent to which the reduction potential of benzoquinone is decreased by the attachment of the benzene ring and of the heterocycle furnishes a means of characterizing quantitatively the relationship between the two cyclic systems.

The interpretation of the results of such a study would be greatly simplified if it were possible to obtain and perform measurements with simple heterocyclic analogs of the naphthoquinones; but it appears that, in the case of certain heterocycles, this is very difficult if not impossible. Both 4,5-indazolequinone[1] and, as we have now found, 1-phenylbenzotriazole-4,5-quinone(I)[2] undergo decomposition too rapidly to permit of satisfactory e.m.f. measurements in alcoholic solution. The destruction of these quinones is undoubtedly due to the 1,4 addition of solvent, acid or a second quinone molecule to the conjugated system, and it can often be prevented by the introduction of a sulfonic acid group in the reactive 4 position. Thus 2-phenylbenzotriazole-4,5-quinone-7-sulfonic acid (II)



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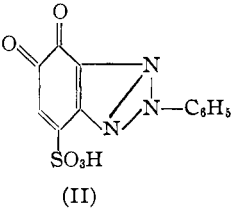


(II)

which was synthesized from 2-phenyl-5-hydroxybenzotriazole was, like indazolequinone sulfonic acid, well suited to the purpose at hand. We were unable, however, to obtain the corresponding 1-phenyltriazole derivative. Unlike many similar *o*-quinones, 1-phenylbenzotriazole-4,5-quinone (I) does not react with sodium bisulfite, so that the direct

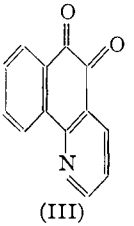
[1] Fieser, THIS JOURNAL, **48**, 1097 (1926).

[2] Fries and Empson, *Ann.*, **389**, 345 (1912).

preparation of the sulfonated hydroquinone could not be accomplished. It was found, moreover, that although 1-phenyl-5-hydroxybenzotriazole readily couples with diazonium salts, it fails to yield a nitroso derivative with nitrous acid, so that the convenient reaction of *o*-nitrosophenols could not be utilized. Further obstacles encountered in the 1-phenyltriazole series are recorded in the Experimental Part.

In view of this experience and because difficulties in the synthesis of other heterocycles were anticipated, it seemed advisable at this time to determine to what extent some of the more readily available heterocyclic quinones would serve to furnish the desired comparison with benzene. To this end a given compound must be at least slightly soluble in alcohol or water, it must be stable in solution and undergo strictly reversible reduction. It is essential, moreover, that sufficient data for related compounds are available in order to interpret the results adequately. In the present study we have examined several known quinones and two new ones from the experimental standpoint and we expect to supply in the future such additional data as now appear necessary for a proper evaluation of some of the results.

Samples of 2-phenyl-α,β-naphthotriazole-4,5-quinone (VI, below)[3] and the isomeric 3-phenyltriazole derivative[4] were kindly furnished for this investigation by Professor Charrier, to whom we wish to express our sincere thanks. Since these compounds, as well as the 1-phenyltriazole isomer,[5] were obtained by the oxidation of the tricyclic analogs of phenanthrene, and since α-naphthoquinolinequinone (III) has been prepared by the oxidation of α-naphthoquinoline,[6] it might be expected that a number of other quinones could be obtained in a similar manner. It appears, however, that the method is not one of very general application.



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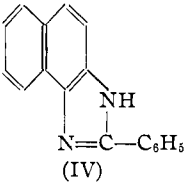

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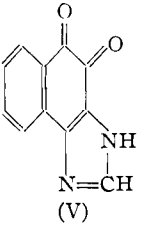


(V)

While α,β-naphthotriazole-4,5-quinone (VIII, below)[7] was readily prepared by the oxidation of α,β-naphthotriazole, no products possessing the properties of a quinone were obtained by the oxidation of 2-methyl-α,β-naphthimidazole[8] or 2-phenylnaphthimidazole (IV).[8] Skraup and

[3] Charrier, *Gazz. chim. ital.*, **54**, 610 (1924).

[4] Charrier, Beretta and Gisella, *ibid.*, **56**, 191 (1926).

[5] Charrier, *Atti accad. Lincei*, (VI), **4**, 312 (1926).

[6] Skraup and Cobenzl, *Monatsh.*, **4**, 461 (1883).

[7] Zincke and Noack, *Ann.*, **295**, 1 (1897).

[8] Fischer, *Ber.*, **34**, 935 (1901).

Cobenzl[6] attempted to convert β-naphthoquinoline into the corresponding quinone but found that oxidation always involved cleavage of the central ring; the experience of Beretta[9] with 2-phenyl-5,6-quinolinetriazole was entirely similar. Although few of the corresponding linear tricyclic compounds appear to have been studied, Fries and Empson report a similar failure to convert N-diphenyl-diethenyl-1,2,4,5-tetra-aminobenzene into a quinone by direct oxidation.[2]

Another method of synthesizing analogs of phenanthrenequinone utilizes 1,2-dihydroxy-3,4-diaminonaphthalene as the starting material.[7]

TABLE I

NORMAL REDUCTION POTENTIALS AT 25°

Compound	Solvent	E_0, v.			ΔE_1, mv.	ΔE_2, mv.	E_0(Av.) v.
2 - Phenylbenzotriazole - 4,5 - quinone - 7-sulfonic acid (II)	0.1 *N* HCl	0.643	0.642		23	18	0.644
	1.0 *N* HCl	.644	.644	0.645	19	17	
2 - Phenyl - α,β - naphthotriazole - 4,5-quinone (VI)	50% alc.	.469	.470	.471	18	25	.470
		.471					
3 - Phenyl - α,β - naphthotriazole - 4,5-quinone (VII)	50% alc.	.514	.512	.514	18	18	.513
α,β-Naphthotriazole-4,5-quinone (VIII)	0.1 *N* HCl	.466	.464	.465	25	21	.465
		.465					
	1.0 *N* HCl	.477	.476		21	24	.477
α-Naphthoquinolinequinone (III)[10]	0.1 *N* HCl	.554	.554		21	20	.554
	1.0 *N* HCl	.560	.560		18	17	.560
	50% alc.	.565	.563		18	19	.564
α,β-Naphthimidazole-4,5-quinone (V)	50% alc.	.529	.527	.527	17	19	.528
		.527					
Phenanthrenequinone[11]	0.1 *N* HCl	.442	.443	.443	29	23	.442
		.439	.443				
	50% alc.	.458	.459	.458	17	19	.458
1 - Phenyl - β,β - naphthotriazole - 4,9-quinone (X)[12]	50% alc.	.259	.256	.253	158	41	(.256)
1 - (*p* - Tolyl) - β,β - naphthotriazole - 4,9-quinone (XI)[13]	50% alc.	.241	.245	.243	63	48	(.244)
		.246					
2 - Methyl - 3 - phenyl - β,β - naphthimidazole-4,9-quinone (XII)[14]	50% alc.	.319	.322	.318	23	23	.320
Thionaphthenequinone (XVIII)[15]	0.1 *N* HCl	.263	.264	.264	18	19	.264
Thiophanthrenequinone (XX)[16]	50% alc.	.250	.250	.249	19	19	.250

[9] Beretta, *Gazz. chim. ital.*, **57**, 179 (1927).

[10] M. p., 206°. Skraup and Cobenzl, Ref. 6.

[11] The value of 0.471 v. for the reduction potential in 95% alcohol, 0.5 *N* in hydrogen chloride, determined by Conant and Fieser, THIS JOURNAL, **46**, 1858 (1924), was also verified.

[12] M. p., 242°. Fries and Billig, *Ber.*, **58**, 1128 (1925).

[13] M. p., 208°. Ref. 12.

[14] M. p., 237°. Ref. 12.

[15] M. p., 116°. Friedländer, *Ann.*, **351**, 399 (1907).

[16] M. p., 227–228°. Steinkopf, *Ann.*, **407**, 99 (1915). The yield of *o*-2-thenoylbenzoic acid was increased to 43% by the use of 2.2 equivalents of aluminum chloride in the Friedel and Crafts reaction.

By condensing this substance with formic acid and oxidizing the product, α,β-naphthimidazole-4,5-quinone (V) was readily obtained.

Determinations of the reduction potentials of the quinones which have been mentioned, and of certain others which are described in the literature, were carried out by electrometric titration with titanous chloride. A hydrogen electrode containing some of the solvent which was used to dissolve the quinone formed the reference half-cell. Measurements were made when possible in aqueous solution, but in most cases the solvent employed was 50% alcohol containing 0.1 mole of hydrogen chloride and 0.2 mole of lithium chloride per liter, the latter electrolyte being added to increase the conductivity of the solution. Though most of the compounds studied dissolve only to a very slight extent in this solvent, no difficulty was experienced in working with the dilute solutions. The results are summarized in Table I. The term "50% alcohol" is used to signify the solution described above. Values found for the normal reduction potentials by interpolation of the titration curves at the point corresponding to half-reduction are given under the heading E_0, while under ΔE_1 and ΔE_2 are given the average differences between E_0 and the potentials at 20% and 80% reduction, respectively. The theoretical value is 17.8 millivolts.

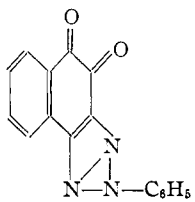
In considering the results, attention may first be called to the fact that the potentials of some of the quinones containing nitrogen increase with increasing acidity of the solution. The variation is probably due to changes in the extent of the basic dissociation of the organic substances.[17] The normal reduction potentials referred to the undissociated oxidant and reductant, which we regard as the most significant for the purpose of correlating reduction potentials and structure, are probably somewhat lower than the values obtained for 0.1 N hydrochloric acid and cannot now be accurately evaluated. In view of this uncertainty, too great significance should not be attached to the exact values of the "normal potentials" of those compounds whose potentials change with acidity. Thus the potential of α-naphthoquinolinequinone in 0.1 N hydrochloric acid is 0.112 v. higher than that of phenanthrenequinone, but the variation with acidity indicates that the difference between the potentials would be less in a solution of such acidity that no dissociation could occur. While it seems unlikely that such a large difference can be due entirely to the effect of ionization, and while the present results thus point to a surprising difference between the pyridine and the benzene nucleus, it is best to reserve judgment on this point until further data are available.

In the case of the phenyltriazole derivatives there is evidence that the results are not influenced by ionization, for the potential of the sulfonated quinone, II, is independent of the acidity of the solution. More

[17] Clark and Cohen, *Pub. Health Repts.*, **38**, 666 (1923).

confidence can thus be placed in the values for this compound and for those similarly constituted.

It will be observed that the values for the normal reduction in 50% alcoholic solution of 2-phenyl-α,β-naphthotriazole-4,5-quinone (VI) and for phenanthrenequinone are very nearly the same. The substitution of the 2-phenyltriazole nucleus for one of the benzene rings in phenanthrenequinone thus produces an alteration in the reduction potential that is scarcely perceptible, which indicates a close relationship between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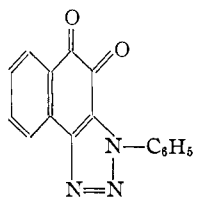
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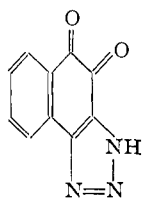
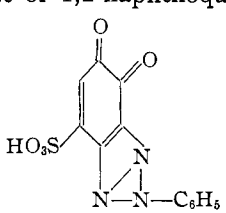

(VIII)

the two cyclic systems. It is important that the same conclusion may be inferred from entirely independent data; the reduction potential of 2-phenylbenzotriazole-4,5-quinone-7-sulfonic acid (II) in aqueous solution is 0.643 v.; that of 1,2-naphthoquinone-4-sulfonic acid (IX) is 0.630 v.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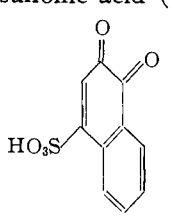
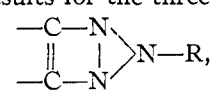
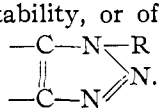
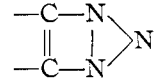

(IX)

That the potentials of the benzenoid quinone and the heterocyclic quinone differ by almost exactly the same amount here as in the tricyclic series is excellent evidence of the general validity of the method and indicates that phenanthrenequinone may be taken as a standard for comparison even though the relationship of the potential to that of β-naphthoquinone is not yet understood.[18]

While 2-phenyl-α,β-naphthotriazole-4,5-quinone (VI) is very similar in potential to phenanthrenequinone, the value for the 3-phenyl isomer (VII) differs by the considerable quantity of 0.047 v. The results for the three compounds indicate that the 2-phenyltriazole system,  , like the benzene ring, represents a condition of greater stability, or of less reactivity and unsaturation, than the isomeric grouping,  .

[18] Conant and Fieser, THIS JOURNAL, 46, 1858 (1924).

On the basis of this evidence, it seems likely that the unsubstituted triazoles, which can conceivably correspond in structure to either of the phenyl derivatives, have the structure of the more stable isomer, namely,  . The reduction potential of the triazolequinone (VIII) lends some support to this conclusion, for it approaches more closely that of the 2-phenyl derivative than that of the isomer. Moreover, since a phenyl group lowers somewhat the potential of benzoquinone,[19] it would be expected that the potential of the true phenyl derivative of naphthotriazolequinone would be perhaps lower, but surely not higher, than that of the parent compound. This relationship is maintained only if the above structure for the triazole ring is adopted.

This structure for the 1,2,3-triazoles was first advanced by Griess,[20] though Zincke[21] showed that the evidence was unsatisfactory. On the other hand, the evidence which led Zincke to favor the double-bond structure does not now appear to exclude definitely the Griess formula.[22] The present results indicate that a reëxamination of this problem is desirable.

Though it is too early to consider the matter in detail, it is of interest to compare briefly our results in the triazole series with those of other investigators. Zincke[23] found that many benzotriazole derivatives were hardly distinguishable from the corresponding naphthalene compounds; Fries,[24] by the extensive application of more definite comparative methods, concluded that the two isomeric phenyl derivatives are exactly similar to each other and to naphthalene. The present work supports these conclusions in a general way, though it points to a difference between the phenyltriazoles. It is of course possible that the electrochemical method reveals differences which are too slight to be detected by a study of the course of substitution reactions; but in view of our results for the pyrazole nucleus[1] and the tentative results for pyridine, it seems more probable that the two methods do not furnish precisely the same information concerning the character of the ring systems in question. For one thing, our method is concerned solely with equilibria, while most of

[19] Private communication from Dr. J. B. Conant.

[20] Griess, *Ber.*, **15**, 1878 (1882).

[21] Zincke, *J. prakt. Chem.*, [2] **53**, 97 (1896).

[22] A third possible structure for benzotriazole, as well as for its 2-N substitution products, involves the "oso-triazole," or quinone-di-imine grouping. Fries, however, has recently shown (*Ann.*, **454**, 137 (1927)) that this structure is inconsistent with the properties of these substances.

[23] Zincke, *Ann.*, **311**, 277 (1900).

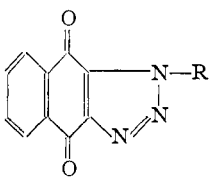
[24] (a) Fries, *Ann.*, **389**, 305 (1912). (b) Fries and Roth, *ibid.*, **389**, 318 (1912). (c) Fries and Empson, Ref. 2. (d) Fries, Sudhoff and Brettschneider, *ibid.*, **454**, 131 (1927).

the methods employed by Fries depend largely upon the relative rates of competing reactions.

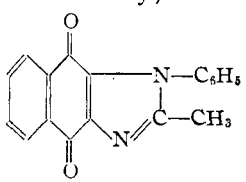
It is of interest that Charrier's statement[4] that 2-phenyl-α,β-naphthotriazole-4,5-quinone is more closely related to phenanthrenequinone in physical properties than the 3-phenyl isomer corresponds with the electrochemical results.

Our results have some bearing on the anomalous relationship between the potentials of some of the benzenoid quinones.[18] Since the attachment of a phenylene group to *o*-benzoquinone lowers its potential by 0.222 v., two such groups would be expected to lower the potential by 0.444 v.; the actual value is considerably less, namely, 0.335 v. In the same way it may be calculated that the attachment of a phenylene group and a 2-phenyltriazole group to *o*-benzoquinone should lower its potential by 0.431 v., if the effects are additive; but the actual value is 0.313 v. The relationship between the compounds of the bi- and tricyclic series is thus the same whether or not one ring is heterocyclic, and it seems probable at the present time that the position of phenanthrenequinone on the potential scale is due to the angular structure of the compound rather than to some peculiar property or structure of the benzene rings of the quinone or its reduction product.

It is important to determine if a similar situation obtains in the series of the linear tricyclic substances such as anthraquinone and its heterocyclic analogs. Unfortunately, the results with the triazole derivatives, X and XI, are not altogether satisfactory; the value for X



X(R = $-C_6H_5$)
XI(R = $-C_6H_4CH_3$)

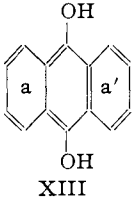


XII

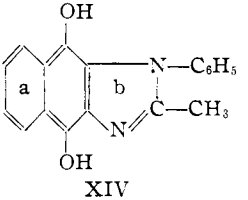
may be as much as 10 mv. too high; that for XI is probably accurate to within 5 mv. However, there can be little doubt as to the general position of the potentials of these compounds, and they may be compared with that of anthraquinone, which is 0.155 v. If compound X were related to anthraquinone in the same way that the angular isomer VII, which also contains the 3(1)-phenyltriazole ring, is related to phenanthrenequinone, the reduction potential of X would be 0.055 v. higher than that of anthraquinone, or 0.210 v.; but the actual value, 0.256 v., is appreciably higher than this. The two imidazole derivatives, V and XII, may be compared in the same way, though they are not isomeric. Since the potential of the angular substance, V, is 0.070 v. above that of phenanthrenequinone, it would be expected that the value for the linear

isomer, β,β-naphthimidazolequinone, would be in the neighborhood of 0.225 v. The potential of the N-methyl-N-phenyl derivative (XII) of this compound should be even lower than this value and, since the actual value is 0.320 v., it seems clear that the assumption that the heterocyclic ring bears the same relationship to the benzene ring in the linear tricyclic compounds as in the angular series does not hold. There seems to be some specific property of the benzenoid and of the heterocyclic rings which only becomes manifest in the linear tricyclic series.

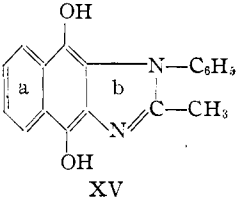
Now the potential of anthraquinone itself is much lower than can be accounted for by supposing that the effect of two phenylene groups attached to *p*-benzoquinone is just twice the effect of one. It is difficult to account for this fact on the basis of the structure of anthraquinone, but it must be remembered that the reduction potential of a quinone is a measure of the free energy of the conversion of the quinone into its hydroquinone and that the structure of the reduction product must also be taken into consideration. The abnormally low potential of anthraquinone may not be due to any peculiarity of the quinone but to some specific property of anthrahydroquinone which renders it particularly reactive and prone to pass over into its oxidation product. It does not appear unwarrantable to consider that this property is due to an orthoquinonoid structure of the hydroquinone, according to Formula XIII,



XIII



XIV



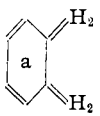
XV

in which Ring a, like the corresponding ring of *o*-benzoquinone, has a tendency to pass into the truly benzenoid condition and so contributes to the reactivity of the molecule as a whole.

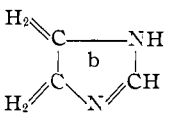
If the Armstrong formulation of anthracene is adopted for heterocyclic analogs of this hydrocarbon, the question arises as to whether Ring a or Ring a′ of XIII has been replaced by the heterocycle, that is, whether it is the benzene ring or the heterocyle which has the quinonoid structure. The problem is similar to the question of the structure of unsymmetrical azines which was explored by Kehrmann[25] and may, in theory, be treated in the same way. If, for example, the ring XIV-a is more reactive than XV-b, the compound will exist chiefly in the form of XV; this form would predominate in the equilibrium mixture. Any nucleus which has the *o*-quinonoid grouping of linkages possesses a certain tendency to rearrange into a more stable structure, but the rearrangement

[25] Kehrmann, *Ber.*, **31**, 977 (1898).

of XIV into XV, which would result if the strained *o*-quinonoid condition of XIV-a is to be relieved, is opposed by the reverse rearrangement due to the tendency of XV-b to pass into a condition of greater stability. Thus an equilibrium between the two forms would result and the point of this equilibrium would depend upon the relative reactivities, in the sense indicated, of the quinonoid rings XIV-a and XV-b. Various methods of estimating these reactivities are conceivable, and one of them is being investigated by Fries.[26] He states that dihydro-imidazole (XVII) is a



XVI



XVII

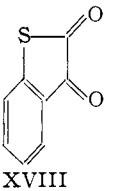
stable substance which is devoid of the tendency to pass into dehydrogenated derivatives which characterizes dihydrobenzene (XVI). Since these two compounds have structures similar to XIV-a and XV-b, it is reasonable to suppose that XV-b is the least reactive of the two and, therefore, that the substance in question corresponds to XV. The substance thus differs from anthrahydroquinone or any other heterocyclic analog in a very essential respect and a simple relationship between these various compounds is not to be expected. From the foregoing analysis we can only say that the linear arrangement of the three nuclei should not result in such a pronounced tendency to undergo oxidation in the case of the heterocyclic substance, XV, as in the case of anthrahydroquinone; in other words, the reduction potential of the quinone corresponding to XV should be higher than that of anthraquinone and higher by an amount not accounted for by the relationship between corresponding angular tricyclic compounds. It is clear that this interpretation agrees with the experimental results.

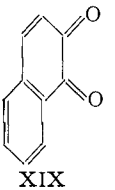
In the case of the triazole derivative, X, the results indicate that the triazole nucleus approximates much more closely the character of the benzene nucleus. The few pertinent chemical facts which are known[26] concerning the triazoles support this conception.

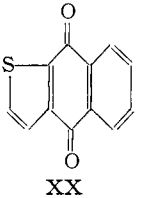
It thus appears highly probable that the specific factor which is operative only in the linear tricyclic series is concerned with the *o*-quinonoid structure of anthracene and its analogs. In order to test this hypothesis further, it is necessary to have some general method of determining the relative tendency of the various cyclic systems to rearrange from the quinonoid into the benzenoid condition. It occurred to us that very precise information on the point in question would be furnished by the determination of the reduction potentials of heterocyclic analogs of *o*-benzoquinone or its derivatives in the event that such determinations

[26] Fries, *Ann.*, **454**, 127 (1927).

are possible. At present, however, very few quinones of the type indicated are known. We have studied one such compound, thionaphthenequinone (XVIII), and have found that it can be brought within the scope of the


XVIII


XIX


XX

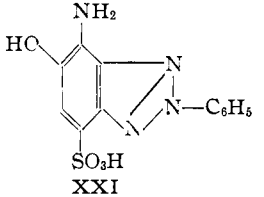
electrochemical method of treatment. Its reduction potential (E_0 = 0.264 v.) is very low in comparison to that of β-naphthoquinone, XIX (E_0 = 0.597 v.). This means that the thiophene ring, present in the reduction product of XVIII, is much more prone to pass into the quinonoid or dihydride condition than is benzene. It is a less stable system.

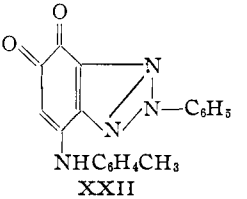
The relatively high potential of thiophanthrenequinone XX (E_0, 0.250 v., as compared with 0.155 v. for anthraquinone) may well be related to this fact, though data on other thiophene derivatives are required before the question can be properly analyzed.

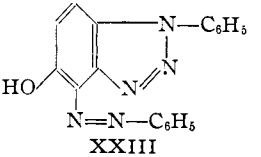
Experimental Part

1. Synthesis of 2-Phenylbenzotriazole-4,5-quinone-7-sulfonic Acid (II).—2-Phenyl-4-nitroso-5-hydroxybenzotriazole, a compound which has been described by Fries and Roth,[24b] formed the starting point for this synthesis. In preparing this substance, 2-phenyl-5-aminobenzotriazole was obtained in 76% yield by reduction of the corresponding nitro compound with stannous chloride,[27] and converted into the hydroxy derivative in the manner described by Fries and Roth, though it was found that the use of boric acid[1] improved the latter process considerably. By the addition of 1.5 molecular equivalents of boric acid to the solution of the diazotized amine before boiling the mixture, the yield was increased from 60% to 85–90% and the time required for the complete evolution of nitrogen was greatly shortened.

2-Phenyl-4-amino-5-hydroxybenzotriazole-7-sulfonic Acid (XXI).—The 4-nitroso derivative prepared from 2.1 g. of 2-phenyl-5-hydroxybenzotriazole was suspended, while still moist, in a solution of 3.1 g. of sodium bisulfite in 150 cc. of water and the


XXI


XXII


XXIII

mixture was stirred for several hours until no more material appeared to go into solution. The solution was then filtered, concd. hydrochloric acid was added in excess, and the solution was allowed to stand at 35° for one day, when the separation of almost colorless crystals of the reaction product had ceased. The substance is very sparingly soluble in

[27] Kehrmann and Messinger, *Ber.*, **25**, 898 (1892). Willgeroth, *J. prakt. Chem.*, [2] **46**, 131 (1892).

water. It dissolves readily in hot sodium bisulfite solution, and on cooling the solution deposits yellow needles of the sodium salt. The free acid was obtained in pure condition, in the form of colorless micro-crystals, from the crystallized sodium salt. It retains combined water even on drying in a vacuum at 100°.[28]

Anal. Calcd. for $C_{12}H_{10}O_4N_4S.1^1/_2H_2O$: C, 43.23; H, 3.93. Found: C, 43.13; H, 3.88.

Potassium 2-Phenylbenzotriazole-4,5-quinone-7-sulfonate (II).—Oxidation of the above compound was accomplished by stirring 1 g. of the material into 2 cc. of 25% nitric acid. On warming slightly all of the material dissolved and orange needles of the ammonium salt of the quinone soon began to separate. After adding saturated ammonium chloride solution and cooling, the precipitate was collected and well washed with ammonium chloride solution. The salt dissolves readily in water and is moderately soluble in alcohol. The potassium salt, which is less soluble, crystallized from water in the form of small, orange-yellow needles.

Anal. Calcd. for $C_{12}H_6O_5N_3SK$: K, 11.39. Found: K, 11.35.

This quinone is very similar in properties to 1,2-naphthoquinone-4-sulfonic acid. It is decomposed by alkalies, giving a green solution from which a red substance precipitates on acidification, while on treatment with concd. sulfuric acid, sulfur dioxide is rapidly evolved and a yellow substance is precipitated on diluting the red, acid solution. The compound is readily reduced by sulfur dioxide and can be condensed with amines. For the purpose of characterization, the *p*-toluidino compound was prepared.

2-Phenyl-7-(*p*-toluidino)-benzotriazole-4,5-quinone (XXII).—A mixture of aqueous solutions of equivalent weights of ammonium 2-phenylbenzotriazole-4,5-quinone-7-sulfonate and *p*-toluidine was heated at the boiling point for ten minutes. The toluidino compound, which was deposited in the form of small, dark red needles, was crystallized from methyl alcohol, in which it is moderately soluble; m. p., 215°.

Anal. Calcd. for $C_{19}H_{14}O_2N_4$: C, 69.07; H, 4.27. Found: C, 69.02; H, 4.42.

2. Experiments in the 1-Phenylbenzotriazole Series.—1-Phenylbenzotriazole-4,5-quinone (I) was prepared by the method of Fries and Empson[2] and crystallized from glacial acetic acid. In addition to the properties reported by these authors, it was noted that, although the quinone is readily reduced by sodium hyposulfite, it is completely insoluble in bisulfite solution. It was also found that nitrous acid is without action on 1-phenyl-5-hydroxybenzotriazole, though this compound couples with diazotized amines.

1-Phenyl-4-benzene-azo-5-hydroxybenzotriazole (XXIII).—To a solution of 2.1 g. of 1-phenyl-5-hydroxybenzotriazole[2] in 25 cc. of water containing 2 g. of sodium hydroxide was added a benzene diazonium chloride solution prepared from 0.93 g. of aniline. After warming for a time and neutralizing the solution, the product was collected and crystallized from alcohol; yield, 2.7 g. (85%). It forms bright red crystals which are sparingly soluble in organic solvents and soluble in alkalies.

Anal. Calcd. for $C_{18}H_{13}ON_5$: C, 68.66; H, 4.16. Found: C, 68.49; H, 4.29.

Attempts to reduce the azo compound to an amine with sodium hyposulfite in alkaline solution were unsuccessful; reduction took place but no product was obtained corresponding in properties to the substance desired.

3. α,β-Naphthotriazole-4,5-quinone.—In preparing this compound according to the directions of Zincke and Noack[7] it was found that β-naphthoquinone, which forms the starting-point of the synthesis, could be most satisfactorily nitrated in the following

[28] Compare the behavior of 1-amino-2-naphthol-4-sulfonic acid, Schmidt, *J. prakt. Chem.*, [2] **44**, 523 (1891).

manner, the success of the process depending largely on having the proper acid concentration. Twenty g. of β-naphthoquinone was stirred into 40 cc. of nitric acid (sp. gr. 1.40) and the mixture was warmed on the water-bath until nitric oxide became apparent and the quinone went into solution (about one minute). The flask was at once transferred to an ice-bath and several small pieces of ice were added. On stirring, crystallization took place almost immediately and after 15 minutes the product was collected and washed successively with concd. nitric acid, glacial acetic acid and ether; yield, 20.6 g. (80%); m. p., 156°. Conversion of this compound, through its hydroquinone, into 3-amino-1,2-naphthohydroquinone was accomplished in 85% yield. We have nothing to add to Zincke and Noack's description of the remaining steps or of the triazole quinone except that this substance, like most *o*-quinones, dissolves readily in sodium bisulfite solution. On adding acid to such a solution, the quinone is apparently reduced by sulfur dioxide, for a salt of the hydroquinone is slowly precipitated.

α,β-Naphthotriazolequinone was also obtained by the oxidation of α,β-naphthotriazole[29] with chromic anhydride in glacial acetic acid solution. Samples prepared in these two ways were purified by crystallization from glacial acetic acid solution and compared by determination of the reduction potential, since the substance has no melting point. The two samples were identical.

4. α,β-Naphthimidazole-4,5-quinone (V).—A mixture of 1 g. of 1,2-diamino-3,4-dihydroxynaphthalene dihydrochloride[7] and 1.1 g. of fused sodium acetate was covered with 85% formic acid and heated under the reflux for one hour. The excess acid was then removed by distillation and the residue dissolved in water. After filtering, the solution was neutralized with ammonia and allowed to stand until separation of the naphthimidazolehydroquinone was complete. The substance was colored bluish-gray due to oxidation; it was not isolated but was at once converted into the quinone by adding it to sufficient nitric acid (sp. gr. 1.4) to bring the material into solution. The orange quinone precipitated on the addition of a small amount of water. When crystallized from alcohol, it formed clusters of orange needles which darken at 210° but remain unmelted at 250°. It is insoluble in benzene or toluene and moderately soluble in alcohol or glacial acetic acid. The solution in concd. sulfuric acid is a deep orange-red; the alkaline solution is rose color. The quinone is readily reduced by sodium hyposulfite and, when the solution in sodium bisulfite is acidified, a salt of the hydroquinone separates.

Anal. Calcd. for $C_{11}H_6N_2O_2$: C, 66.66; H, 3.05. Found: C, 66.50, H, 3.17.

5. E.m.f. Measurements.—The results given in Table I were obtained by measuring the potential difference between a half-cell containing the quinone-hydroquinone solution and a hydrogen electrode half-cell containing the same solvent. The potentiometer was accurate to 0.5 mv. Titanous chloride solutions, containing approximately from 0.03 to 0.4% of this reagent, were prepared from the 20% standardized solution immediately before each determination. In those cases in which the solubility of the quinone is very slight, the solution was prepared by digesting an excess of the quinone with 300 cc. of the solvent at 60°, cooling to 20° and filtering. Judging from the solubility of phenanthrenequinone in water, which is 3.6×10^{-5} at 25°,[30] the solutions of the quinones ranged in molar concentration from about this value to about 1×10^{-3}. The concentration of titanous chloride required to furnish a titration curve of suitable dimensions was determined in a preliminary experiment.

Most of the measurements require little comment, though it may be noted that with all of the compounds, with the exception of the first one listed in Table I, constant

[29] Diels, *Ber.*, **54**, 226 (1921).

[30] Knox and Will, *J. Chem. Soc.*, **115**, 850 (1919).

potentials were reached only after considerable periods of time, and a complete titration often required three or four hours. In the case of the 2-phenylbenzotriazole-4,5-quinone-7-sulfonic acid, electrode equilibrium was established with great rapidity in aqueous solution, but the measurements in alcoholic solution were unsatisfactory because of the decomposition of the quinone. The first few points of the titration curve, instead of forming the usual inflection, fell on a straight line which included the point corresponding to the potential of the solution before any reducing agent had been added. This is clear evidence of the reaction of the quinone and the solvent with the production of reduction products and this conclusion is supported by the fact that the potential at half-reduction was not reproducible and was much lower than the value which might reasonably be predicted for the normal potential. Titration curves of exactly similar characteristics were obtained with 1-phenylbenzotriazole-4,5-quinone (I) and the results were consequently rejected.

A curious behavior was observed in carrying out measurements with 1-phenyl-β,β-naphthotriazole-4,9-quinone (X). On adding an increment of titanous chloride solution, the e.m.f. of the cell very slowly changed to a less positive value and finally became constant. When the quinone had been about half reduced, equilibrium was established much more rapidly, but somewhat beyond this point the cell potential fell in the normal manner after the addition of the reducing agent, remained poised at a constant value for a few minutes, and then began to rise. The effect was particularly evident toward the final stages of reduction. This behavior may be due to the action of the reducing agent on parts of the molecule other than the quinone grouping. By carrying out rapid titration in which the "poised potentials" were recorded, values for the normal potential were obtained which are probably not greatly in error, though the slopes of the titration curves, indicated by ΔE_1, deviated widely from the theoretical. In the case of the *p*-tolyltriazole derivative XI the situation was similar, though the potentials did not rise as rapidly as before and the results are somewhat more accurate.

Since thionaphthenequinone is the first substance of its type which has been found to give, in mixtures containing its reduction product, definite electrode potentials which conform to the usual electrochemical equation, it seems advisable to include further details concerning our experiments with this compound than are given in Table I. The results of a typical titration, together with the values for the normal potential which have been calculated from the equation $E_0 = E_{cell} - 0.0296 \log [Oxid.]/[Red.]$, are given in Table II. The oxidation-reduction half-cell

TABLE II

TITRATION OF THIONAPHTHENEQUINONE IN 0.1 *N* HCl SOLUTION WITH $TiCl_3$. END POINT = 8.70 CC. E_0 BY GRAPHICAL INTERPOLATION = 0.2635 V.

$TiCl_3$, cc.	E_{cell}, v.	E_0 (calcd.), v.	$TiCl_3$, cc.	E_{cell}, v.	E_0 (calcd.), v.
0.0	(0.571)	...	4.0	0.2655	0.2634
.5	.314	(0.278)	4.5	.2625	.2634
1.0	.294	(.268)	5.0	.2955	.2633
1.5	.2850	.2648	6.0	.2528	.2631
2.0	.2790	.2635	7.0	.2440	.2622
2.5	.2745	.2628	8.0	.226	(.277)
3.0	.2716	.2634	8.5	.196	(.244)
3.5	.2683	.2639	8.7	.125	...

Av. = 0.2634 v.

contained a gold-plated and a platinized platinum electrode, both of which were always used in making the readings. While with most compounds the two readings usually agree well, it was found that with thionaphthenequinone the gold-plated electrode easily became polarized and that the potentials recorded were inconstant, irreproducible and differed from those recorded on the platinized electrode, which behaved in normal fashion, by 2–10 mv. These readings were disregarded. No consistent results were obtained with either type of electrode in alcoholic solution.

We wish to acknowledge our indebtedness to the Cyrus M. Warren Fund of the American Academy of Arts and Sciences for a grant used to purchase the electrical instruments employed in this work.

Summary

1. On comparing the reduction potentials of the quinones of the naphthalene and phenanthrene series with quinones containing the 2-phenyltriazole nucleus in place of one of the benzene rings, it has been found that a striking similarity exists between this heterocyclic nucleus and benzene. The 1,2,3-triazole ring is similar to these other two and probably has the structure of the 2-phenyl derivative, for a quinone containing the 3-phenyltriazole grouping is much higher in potential than the corresponding triazolequinone or its 2-phenyl derivative.

2. Preliminary results indicate that the pyridine and the imidazole nuclei do not produce a lowering in the potential of quinones to which they are attached which is at all comparable with the effect of a phenylene group.

3. Heterocyclic analogs of anthraquinone do not bear the same relation to this substance which the angular isomers bear to phenanthrenequinone. A tentative explanation of these facts, based upon the *o*-quinonoid theory of the structure of anthracene, has been suggested.

4. The reduction potential of thionaphthenequinone, the first substance of its type to which the electrochemical method has been successfully applied, has been determined in aqueous solution.

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