monium hydrogen sulfite, leaving the iron and zinc in solution.

Aluminum is separated as $AlCl_3 \cdot 6H_2O$ from a hydrogen chloride saturated ether–water mixture in which gallium and traces of iron remain dissolved.

After the remaining iron has been removed, the gallium is precipitated as the hydrated oxide. The metal is obtained by electrolysis from a solution of the oxide in potassium hydroxide solution.

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A Comparison of Heterocyclic Systems with Benzene. V. The Benzotriazole (Azimidobenzene) Series

BY LOUIS F. FIESER AND ELMORE L. MARTIN

Since only one, rather unfavorable, example of a quinone containing the 1,2,3-triazole nucleus has been studied potentiometrically,[1] the synthesis of simple ortho or para quinones derived from benzotriazole was undertaken in order that a direct comparison might be made with the naphthoquinones. Although it was found that the benzotriazole quinones are unusually elusive substances, we were able to produce one member of the series in solution and to obtain from it the pure, crystalline hydroquinone. This was well suited to the purpose at hand.

The starting point for the preparation was 5-hydroxybenzotriazole, V, a compound which was unknown at the beginning of our investigation, but which has been described by Fries, Güterbock and Kühn[2] in a paper published since the completion of this part of our work. The Fries group prepared the hydroxy compound from the amine, the starting point for the preparation of which is 2,4-dinitroaniline. From the statements in the literature, supplemented by observations of our own, it is estimated that the over-all yield by this method is about 18%. We selected for the synthesis the series of transformations I → V.
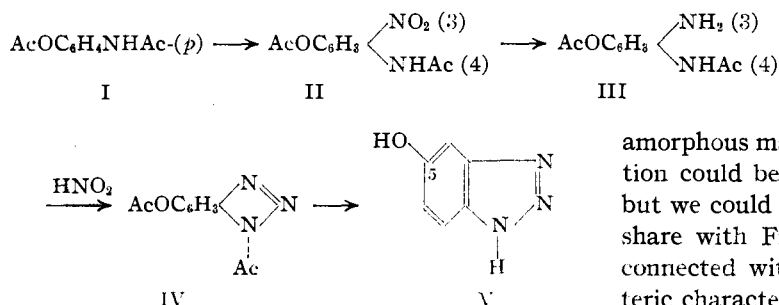
Reduction of the nitro compound II could not be accomplished with stannous chloride or sodium hydrosulfite without hydrolysis, but catalytic hydrogenation to the amine III proceeded smoothly, with a small amount of the hydrazo compound as the only by-product. The remaining steps were nearly quantitative, and the yield from p-aminophenol was 53%.

As a means of introducing an amino group in the 4-position, the reduction of the arylazo, nitro, and nitroso derivatives of 5-hydroxybenzotriazole was studied under various conditions. All of these substances gave the same reduction product, VI, but the only satisfactory preparative method consisted in the reduction of the nitroso compound with sodium hydrosulfite in a neutral,
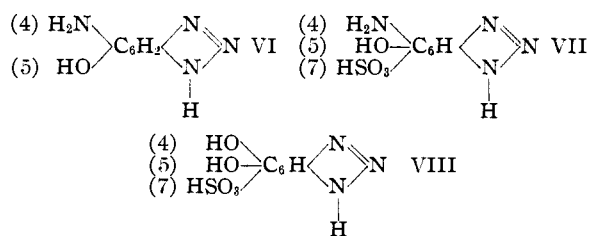
aqueous suspension. Like Fries and collaborators, who were the first to prepare 4-amino-5-hydroxybenzotriazole, we were unable to isolate a quinone on oxidation of the substance. Under ordinary conditions only black, amorphous material was obtained. A red coloration could be produced in very dilute solutions, but we could not isolate the red substance. We share with Fries the view that the difficulty is connected with the water solubility and amphoteric character of the unknown quinone.

From the 4-nitroso derivative we obtained with bisulfite 4-amino-5-hydroxy-7-sulfonic acid,

(1) Fieser and Ames, THIS JOURNAL, 49, 2604 (1927).
(2) Fries, Güterbock and Kühn, Ann., 511, 213 (1934).

VII, and the oxidation of this substance was somewhat more successful. Clear orange-red solutions could be obtained which responded to the usual tests (with aniline, alkali, etc.) for an ortho quinone sulfonate, but the substance appears to be extremely soluble in water and rather sensitive, and we were unable to isolate it. To prepare the hydroquinone, VIII, the sulfonate VII was oxidized with bromine water and the red solution was decolorized with sulfur dioxide. 4,5-Dihydroxybenzotriazole-7-sulfonic acid (VIII) was obtained as colorless crystals of the potassium salt.

As a possible route to a quinone of the para series, we investigated Gattermann's method of preparing p-aminophenols by the electrolytic reduction of nitro compounds in concentrated sulfuric acid solution. Benzotriazole, the required starting material, usually is prepared by the action of nitrous acid on o-phenylenediamine. A more economical method, which has advantages with respect both to the yield and the quality of the product, consists in diazotizing o-aminoacetanilide and hydrolyzing the resulting acetate. To obtain o-aminoacetanilide, o-nitroaniline was acetylated in benzene solution by a method similar to that of Kaufmann,[3] and the nitro compound was reduced catalytically. In each of the five operations involved in the new synthesis of benzotriazole the yield was 90% or better, and pure products were easily obtained at each step. In the hydrogenation of o-nitroacetanilide, small amounts of the hydrazo compound and of 2-methylbenzimidazole were formed, but these substances are easily eliminated. Fries and collaborators[2] showed that the nitration of benzotriazole yields the 4-nitro compound. We were able to transform this substance into 4-amino-7-hydroxybenzotriazole, but all attempts to isolate a quinone by the oxidation of the compound were unsuccessful. No better results were obtained with the known methylated nitrobenzotriazoles. With 1 - methyl - 4 - nitrobenzotriazole the Gattermann reaction was successful, but no quinone could be obtained on oxidation. No pure product was isolated from the electrolytic reduction of 1-methyl-7-nitrobenzotriazole.

Potential Measurements

Solutions of benzotriazole-4,5-quinone-7-sulfonate (XI) prepared by the oxidation of the pure

(3) Kaufmann, *Ber.*, **42**, 3481 (1909).

hydroquinone VIII in dilute aqueous solution were found to be quite stable at 25° except in strongly alkaline solutions. The results of a series of electrometric titrations of the reductant, carried out by the method previously described,[4] and under the same conditions, are summarized in Table I. Bromine water proved to be an excellent titrating agent for the acid and neutral range, electrode equilibrium being attained very rapidly.

TABLE I

POTENTIALS OF THE SYSTEM FROM POTASSIUM BENZOTRIAZOLE-4,5-QUINONE-7-SULFONATE (25°)

$E_0 = 0.6721$ v.　$K_o^b = 1.04 \times 10^{-5}$.　$K_r^b = 1.57 \times 10^{-6}$.
$E_n = E_0 + E_h + 0.02956 \log [1 + [H^+]/K_r^b] - 0.02956 \log [1 + [H^+]/K_o^b]$.

pH	Hydrogen elec. potential, E_h, v.	Potential when Ox. = Red., E_n, v.	Titrating agent	E_n (found − calcd.), mv.
0.50	−0.0296	0.6667	Br₂-H₂O	−0.1
1.15	.0680	.6284	Br₂-H₂O	.0
3.27	.1933	.5037	Br₂-H₂O	+ .6
4.31	.2548	.4415	Br₂-H₂O	− .1
4.31	.2548	.4420	K₃Mo(CN)₈	+ .4
4.95	.2926	.3962	Br₂-H₂O	− .8
5.34	.3157	.3691	Br₂-H₂O	− .1
5.68	.3358	.3469	Br₂-H₂O	+1.9
6.13	.3624	.3136	Br₂-H₂O	−0.2
6.65	.3931	.2784	Br₂-H₂O	− .6
6.99	.4132	.2587	Br₂-H₂O	− .2
7.62	.4505	.2223	Br₂-H₂O	+ .7
7.78	.4599	.2128	Br₂-H₂O	+ .6
8.35	.4937	.1778	K₃Mo(CN)₆	− .6
8.89	.5256	.1588	K₃Mo(CN)₆	...

The normal potential (E_0) for the system of which the heterocyclic quinone XI is the oxidant is 42 mv. higher than that for the carbocyclic quinone XII. This comparison is regarded as

$E_0 = 0.672$ v.
XI

$E_0 = 0.630$ v.
XII
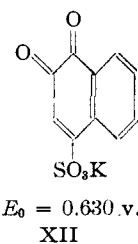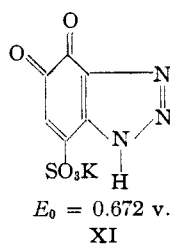
more accurate than that between α,β-naphthotriazole-4,5-quinone and phenanthrenequinone (difference of 23 mv.),[1] for the factor of dissociation could not be taken into account in the earlier work. According to the present results there is a difference of nearly one pK unit in the constants for the basic ionization of the triazole nucleus in the quinone and in the hydroquinone, the latter

(4) Fieser and Fieser, This Journal, **56**, 1565 (1934).

substance being the more strongly basic. The normal potential (E_0) reported refers to conditions under which there is no basic ionization of either the oxidant or the reductant. The value is intermediate between those for the quinones containing a benzene ring and a thiophene ring[5] in place of the triazole nucleus. If the comparison is strictly valid, this would indicate an intermediate degree of aromaticity for the triazole system, this ring being less aromatic than benzene.

Experimental Part

1. Synthesis of 5-Hydroxybenzotriazole (V)

1 - Acetylamino - 2 - nitro - 4 - acetoxybenzene.[6]—1 - Acetylamino-4-acetoxybenzene, m. p. 150–151°, was obtained from p-aminophenol hydrochloride in 90% yield. For the nitration, 100 g. of the diacetate was added in small portions to 200 cc. of fuming nitric acid (sp. gr. 1.5) which was mechanically stirred in a freezing mixture. The temperature was kept at 0–5° throughout the addition which, with efficient cooling, required fifteen to twenty minutes. The temperature was allowed to rise to 12–15° and maintained there for twenty to twenty-five minutes, when the solution was poured onto ice. The yellow product was washed entirely free from acid and crystallized from alcohol, when it formed stout yellow needles, m. p. 144–145°; yield, 110 g. (89%).

1-Acetylamino-2-amino-4-acetoxybenzene (III).—The hydrogenation was carried out in the low pressure apparatus, using 30 g. of the nitro compound dissolved in 300 cc. of hot alcohol and 0.1 g. of Adams catalyst. With a good catalyst the temperature rose and the reduction was complete in ten to fifteen minutes. The colorless solution was filtered and the solvent was distilled in vacuum, giving a slightly yellow crude product melting at 172–174°; yield from a total of 120 g., 98 g. (93%). This contained as a by-product the orange azo compound, which was left as a residue on dissolving the crude amine in hot water. On decolorizing the solution and cooling, the amine was obtained as colorless plates, m. p. 175–177°; yield 79 g. (75%). The pure compound crystallizes from water in fine needles, from alcohol as square plates, m. p. 178–179° (Analysis No. 1, Table II).

The following derivatives were obtained in somewhat purer form than by previous methods. 1,2-Di-(acetylamino)-4-acetoxybenzene was prepared by acetylating III in aqueous solution and crystallized from water (No. 2): fine needles, m. p. 187–188° (lit., 184–185°).[7] 3,4-Di-(acetylamino)-phenol was obtained by treatment of the triacetate with cold, dilute alkali for one hour and acidifying the resulting solution (No. 3): stout needles from water, m. p. 214–215° (lit., 205–207°).[7]

2,2' - Di - (acetylamino) - 5,5' - diacetoxyazobenzene (No. 4) appeared in amounts of 0.1–1.0 g. in each hydrogenation of 30 g. of the nitro compound, the quantity being greatest when the catalyst was poor and the reduction slow. The substance is not present as such at the end of the hydrogenation but as the hydrazo compound, which becomes oxidized after exposure to the air. The azo compound is insoluble in acids or alkalies and it crystallizes from glacial acetic acid (sparingly soluble) as fine orange needles decomposing at 280–285°.

1-Acetyl-5-acetoxybenzotriazole, IV (No. 5).—To a solution at 0° of 62.4 g. of the pure amine III in 53 cc. of concentrated hydrochloric acid and 750 cc. of water, a solution of 20.7 g. of sodium nitrite in 200 cc. of water was slowly added. The triazole separated at once to give a crystalline paste and it was collected and washed; m. p. 125°; yield, 64 g. (98%). The substance was obtained from benzene–ligroin or from dilute acetone as fine, colorless needles, m. p. 125–126°. From 5-hydroxybenzotriazole and acetyl chloride in pyridine Fries, et al.[2] obtained a diacetate which sintered at 115° and melted at 127°. With acetic anhydride and sodium acetate we obtained a sample identical with the above. Unlike the case of 5-methylbenzotriazole[8] the acetylation gives only one of the two possible isomers.

5-Hydroxybenzotriazole Hydrochloride (No. 6).—The moist diacetate obtained as above (64 g., dry) was warmed with 200 cc. of concentrated hydrochloric acid until solution was complete (a slight yellow color was discharged if necessary by the addition of a trace of stannous chloride). On cooling to 0° 43 g. of colorless crystals separated, and 4 g. more was obtained by concentrating the mother liquor; yield, 90%. For analysis the compound was recrystallized from dilute acid, when it formed stout, colorless needles decomposing at about 225°.

5-Hydroxybenzotriazole, V (No. 7).—On mixing aqueous solutions of 5.15 g. of the above hydrochloride and of 2.6 g. of sodium bicarbonate a white, crystalline precipitate began to form after a few minutes; m. p. 232–234°; yield, 3.6 g. (90%). The compound crystallized from water as colorless micro-needles, m. p. 234–235°, with some decomposition. Fries, et al.[2] obtained a slightly yellow product, m. p. 228° dec.

2. Derivatives of 5-Hydroxybenzotriazole

The 4-benzeneazo derivative (No. 8), orange needles from alcohol, m. p. 230–232°, dec., the 4-p-tolueneazo compound (No. 9), reddish-orange needles from alcohol, m. p. 224–225°, and the 4-o-tolueneazo compound (No. 10), bright red needles from alcohol, m. p. 243–244° dec., were prepared in the usual way. The dyes are insoluble in dilute hydrochloric acid but soluble in alkali (probably because of the acidic character of the triazole nucleus).

4-Nitro-5-hydroxybenzotriazole (No. 11).—To a solution of 10.8 g. of III in 40 cc. of concentrated sulfuric acid at 15–20° 4 cc. of nitric acid (sp. gr. 1.4) was added by drops. After one-half hour at 15–20° and one hour at 50°, the solution was poured onto ice, and the product was crystallized from dilute acetic acid; m. p. 262–263°; yield, 9 g. (63%). Fries, et al.[2] prepared the compound by another method and give the melting point as 236° dec. This probably is a typographical error.

4-Nitroso-5-hydroxybenzotriazole (No. 12) was prepared by a method similar to that of Fries, et al.:[2] sodium nitrite solution was added to a solution of 5-hydroxybenzotriazole hydrochloride in water; yield, 97%.

(5) Fieser and Kennelly, THIS JOURNAL, **57**, 1611 (1935).

(6) Hähle, J. prakt. Chem., **43**, 63 (1891), prepared this compound but recorded few details of the procedure.

(7) Kehrmann and Gauhe, Ber., **31**, 2404 (1898).

(8) Morgan and Micklethwait, J. Chem. Soc., **103**, 1396 (1913).

4 - Amino - 5 - hydroxybenzotriazole - 7 - sulfonic Acid (VII).—The moist nitroso compound from 5.16 g. of 5-hydroxybenzotriazole was stirred for one hour with a solution of 8.8 g. of sodium bisulfite in 200 cc. of water, when it all dissolved. The filtered, yellow solution was treated with 10 cc. of concentrated sulfuric acid and maintained at 40° for three and a half hours. The solution had become red and a yellow, crystalline product had separated. This was dissolved in a hot solution of 10 g. of sodium bisulfite in 50 cc. of water, the solution was decolorized with Norite and acidified while still hot. The product was pale yellow and weighed 4.8 g. (70%). The color was removed completely by crystallization from water, in which the substance is only sparingly soluble. The compound separates slowly in long, colorless needles; it dissolves in alkali or soda with a green coloration.

Anal. Calcd. for $C_6H_6O_4NS$: S, 13.92. Found: S, 13.94, 14.01.

Potassium Benzotriazole-4,5-hydroquinone-7-sulfonate (VIII).—Of various oxidizing agents tried for the preparation from VII of solutions of the triazolequinone sulfonate, bromine water was the most satisfactory. In the presence of an excess of bromine the orange solution is fairly stable. Treated with alkali, the solution becomes dark and then clear red. With aniline a red anilino quinone is precipitated, but the compound was not obtained in a crystalline condition. The hydroquinone was obtained as follows. A small part of 3.3 g. of VII was suspended in 10 cc. of water and shaken with a small part of 1 cc. of bromine. The material soon dissolved to give an orange solution, and further small quantities of the aminohydroxy compound and of bromine were added with shaking until all had been used. To the filtered quinone solution 10 cc. of saturated potassium chloride solution was added, and the solution was decolorized with sulfur dioxide. The potassium salt VIII began to separate at once as colorless crystals. When crystallized from water containing a little sulfur dioxide the substance formed stout, glistening needles of the tetrahydrate; yield, 2.6 g. (55%).

Anal. Calcd. for $C_6H_4O_5N_3SK\cdot4H_2O$: S, 9.67. Found: S, 9.62, 9.65.

4-Amino-5-hydroxybenzotriazole.—(a) To a saturated aqueous solution of 10.5 g. of sodium hydrosulfite 3.28 g. of 4-nitroso-5-hydroxybenzotriazole was added slowly with stirring. The mixture became warm and the yellow solid soon was transformed to the colorless, crystalline reduction product. Crystallized from hot water containing a trace of hydrosulfite, this gave 2.5 g. (83%) of the free amine, m. p. 210–214° dec., and from it 3 g. of the pure, colorless dihydrochloride was obtained.

(b) The 4-benzeneazo compound was reduced with stannous chloride and the tin double compound was decomposed with hydrogen sulfide. The dihydrochloride was obtained by evaporation in vacuum; yield, 22%.

(c) Electrolytic reduction of the 4-nitro compound (7 g.) in concentrated sulfuric acid gave 10 g. of the amino-hydroxybenzotriazole as the sparingly soluble sulfate.

That these three methods give the same product was shown by a comparison of samples of the free base, which is best prepared from the pure dihydrochloride by the addition of sodium bicarbonate, followed at once by a trace of hydrosulfite, to the aqueous solution of the salt. 4-Amino-5-hydroxybenzotriazole (No. 13) crystallizes from water as long, colorless needles, m. p. 216–217° dec. Fries, *et al.*,[2] report the m. p. 217°. The substance soon darkens when exposed to the air in a moist condition. The **dihydrochloride (No. 14)** was obtained as completely colorless, stout needles, decomposing at about 225°; it does not deteriorate on storage.

3. Preparation of Benzotriazole

2-Nitroacetanilide.—To a solution of 69 g. of *o*-nitroaniline in 75 cc. of warm benzene 75 cc. of acetic anhydride was added, along with 3–5 drops of concentrated sulfuric acid. The latter reagent initiated a vigorous reaction and a part of the benzene distilled. After heating on the steam-bath for thirty minutes, the solvent was removed by evaporation in a dish on the steam-bath, and on cooling the light yellow melt solidified. One crystallization from dilute alcohol gave 84 g. (93%) of yellow needles, m. p. 92–93°.

2-Aminoacetanilide.—Hydrogenation of the nitro compound (30 g. in 200 cc. of hot alcohol, with 0.1 g. of Adams catalyst) proceeded smoothly (ten to fifteen minutes), and on evaporation of the filtered, initially colorless solution in vacuum the crude amine was obtained as a slightly yellow product, m. p. 130–132°. From 120 g. of nitro compound the yield was 97 g. (97%). The main portion dissolved readily in hot water, leaving a yellow residue which, when crystallized from glacial acetic acid, formed orange needles, m. p. 270–271°, having the properties of 2,2'-di-[acetylamino]-azobenzene.[9] On clarifying and cooling the aqueous solution, 2-aminoacetanilide (75 g.) separated as colorless plates, m. p. 132–133°, and an additional crop was obtained by concentrating the mother liquor under reduced pressure; yield, 90 g. (90%). A second concentration of the mother liquor gave 3 g. of another substance which, when recrystallized from water, melted at 174–175°, corresponding with the description of 2-methylbenzimidazole.[10]

1-Acetylbenzotriazole.—A solution at 0° of 100 g. of pure 2-aminoacetanilide in 500 cc. of water and 120 cc. of concentrated hydrochloric acid was treated with a solution of 46 g. of sodium nitrite in 200 cc. of water, added dropwise with stirring. A colorless precipitate separated at once; washed and dried it weighed 102 g. (95%) and melted at 49–51° (recrystallized, 50–51°).

Benzotriazole.—The crude acetate (100 g.) was dissolved by warming in 150 cc. of concentrated hydrochloric acid, a small crystal of stannous chloride being added to remove a slight yellow coloration. On cooling, colorless needles of the hydrochloride separated (82 g.), and a further crop was obtained by concentration of the mother liquor; yield, 89 g. (92%). A solution of 46.7 g. of the pure salt in 200 cc. of water was carefully neutralized with a solution of 26 g. of sodium bicarbonate. Benzotriazole separated as colorless crystals, m. p. 97–98°; yield, 33 g. (92%). Recrystallization from benzene gave long, colorless needles, m. p. 98–99°.

The preparation of benzotriazole by the action of nitrous acid on *o*-phenylenediamine was found to be quite tedious in comparison with the above method. After three treat-

(9) Willstätter and Pfannenstiel, *Ber.*, **38**, 2351 (1905).

(10) Hübner, *Ann.*, **209**, 353 (1881).

ments with Norite we obtained a light gray product, m. p. 94–96°, in 67% yield.

4. Electrolytic Reduction of the Nitro Compounds

4-Amino-7-hydroxybenzotriazole (No. 15).—4-Nitrobenzotriazole was prepared by nitration essentially as described by Fries, et al.,[2] the yield of recrystallized material, m. p. 229–230°, being 68%. A solution of 10 g. of the nitro compound in 100 g. of concentrated sulfuric acid was subjected to electrolytic reduction according to Gattermann,[11] using a 5 × 9 cm. porous clay cell resting in a beaker of 80–90% of sulfuric acid. The current, taken from a 6-v. line, increased from 1–1.5 amp. to about 3 amp. as the temperature rose to the maximum value of 70–80°. The reaction was complete in about twenty hours and a part of the amine sulfate separated during this period and the remainder was obtained by diluting the acid liquor with an equal volume of water and allowing the solution to stand at 0° for two days; yield, 10 g.

The sulfate is sparingly soluble in water and it does not crystallize well. The free base was liberated from the salt with sodium bicarbonate and crystallized from water in the presence of a trace of sodium hydrosulfite. The colorless needles were collected, washed with alcohol and ether, and quickly dried in vacuum. The substance decomposes at about 225–230°, and it is sensitive to air oxidation. It is moderately soluble in water, sparingly soluble in ether. Oxidizing agents added to a solution of the hydrochloride produce a red coloration, but no quinone could be isolated.

1-Methyl-4-nitrobenzotriazole.—Following the method of Fries, et al.,[2] 4-nitrobenzotriazole was methylated with dimethyl sulfate. Like their material, our product softened at 163° and melted at 173° even after several crystallizations from alcohol, but after a single crystallization from dilute acetic acid the substance melted sharply at 181–182° and this value remained unchanged on further crystallization. The yield of the pure isomer was 30%.

1-Methyl-4-amino-7-hydroxybenzotriazole was obtained in good yield by reduction of the 4-nitro compound by the Gattermann method. The sulfate forms colorless micro crystals and is moderately soluble in water. The free base is very sensitive to oxidation and was not obtained entirely pure. The **dibenzoate** (No. 16) forms colorless needles from alcohol, m. p. 262–263°.

(11) Gattermann, Ber., **26**, 1846 (1893).

1-Methyl-7-nitrobenzotriazole.—The methylation of benzotriazole by Reissert's[12] method gave the 1-methyl derivative in less than 10% yield. The nitro compound[2] gave no clean products when submitted to electrolytic reduction in sulfuric acid solution.

TABLE II
ANALYSES[13]

No.	Formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
1	$C_{10}H_{12}O_3N_2$	57.67	5.81	57.64	6.06
2	$C_{12}H_{14}O_4N_2$	57.58	5.64	57.29	5.40
3	$C_{10}H_{12}O_3N_2$	57.67	5.81	57.88	5.97
4	$C_{20}H_{20}O_6N_4$	58.23	4.89	58.00	5.24
5	$C_{10}H_9O_3N_3$	54.78	4.14	54.72	4.50
6	$C_6H_6ON_3Cl$	41.68	3.52	41.91	3.83
7	$C_6H_5ON_3$	53.31	3.73	53.37	4.04
8	$C_{12}H_9ON_5$	60.23	3.79	60.23	3.86
9	$C_{13}H_{11}ON_5$	61.64	4.38	61.51	4.38
10	$C_{13}H_{11}ON_5$	61.64	4.38	61.64	4.44
11	$C_6H_4O_3N_4$	39.98	2.24	40.37	2.12
12	$C_6H_4O_2N_4$	43.89	2.46	44.05	2.74
13	$C_6H_6ON_4$	47.97	4.03	48.09	4.42
14	$C_6H_6ON_4Cl_2$	32.29	3.62	32.35	3.73
15	$C_6H_6ON_4$	47.97	4.03	48.12	4.27
16	$C_{21}H_{16}O_3N_4$	67.71	4.33	67.79	4.73

Summary

Methods of obtaining ortho and para quinones or hydroquinones of the benzotriazole series have been investigated and one compound of the type desired has been prepared and studied potentiometrically. The oxido-reduction potential of a bicyclic quinone containing the triazole nucleus is appreciably higher than that of the corresponding naphthoquinone.

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(12) Reissert, ibid., **47**, 677 (1914).

(13) The semimicrocombustion of some of these compounds, particularly those containing the stable triazole nucleus and having a high nitrogen content, presented considerable difficulty. The method found most satisfactory was to mix the sample with fine copper oxide and to conduct the combustion with air in a very hot tube.