atom makes the acid much more stable toward water. We might expect that the introduction of the third chlorine atom would also have this same effect but in this case the hydrolysis is not a true hydroxylation. From the table it is evident that trichloroacetic acid is the most unstable of the acids discussed in this paper.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

BROMOHYDROXYNAPHTHOQUINONES.[1]

BY A. S. WHEELER AND V. C. EDWARDS.

Received August 13, 1917.

In our study of the 1,4,5,6-tetrahydroxynaphthalene we proved that this compound is a quinone as well as a phenol, since it readily forms a semicarbazone, a phenylsemicarbazone and similar characteristic ketone derivatives. A somewhat analogous case is found in the hydrojuglons. When juglon is reduced with zinc dust to hydrojuglon, the product is almost wholly a trihydroxyphenol and this can be converted by melting almost wholly into the keto form. Willstätter and Wheeler[2] cleared up the constitution of these hydrojuglons by showing that they present a case of keto enol isomerism. The tetrahydroxynaphthalene, which is obtained by the reduction of naphthazarine by stannous chloride, presents a somewhat different case in that the two isomeric forms cannot be separated from each other, resembling in this respect phloroglucinol. The tetrahydroxynaphthalene was known to give readily a tetracetate and we have shown in Part I that it gives readily a series of ketone derivatives.

With a view to a deeper study of this case of tautomerisn, we attacked the problem of the bromination of naphthalene. This has opened up a very interesting field and in spite of one or two unsettled questions in the work so far done, it becomes necessary to publish our results because one of us[3] has entered the industrial field, thus severing permanently our co-operation.

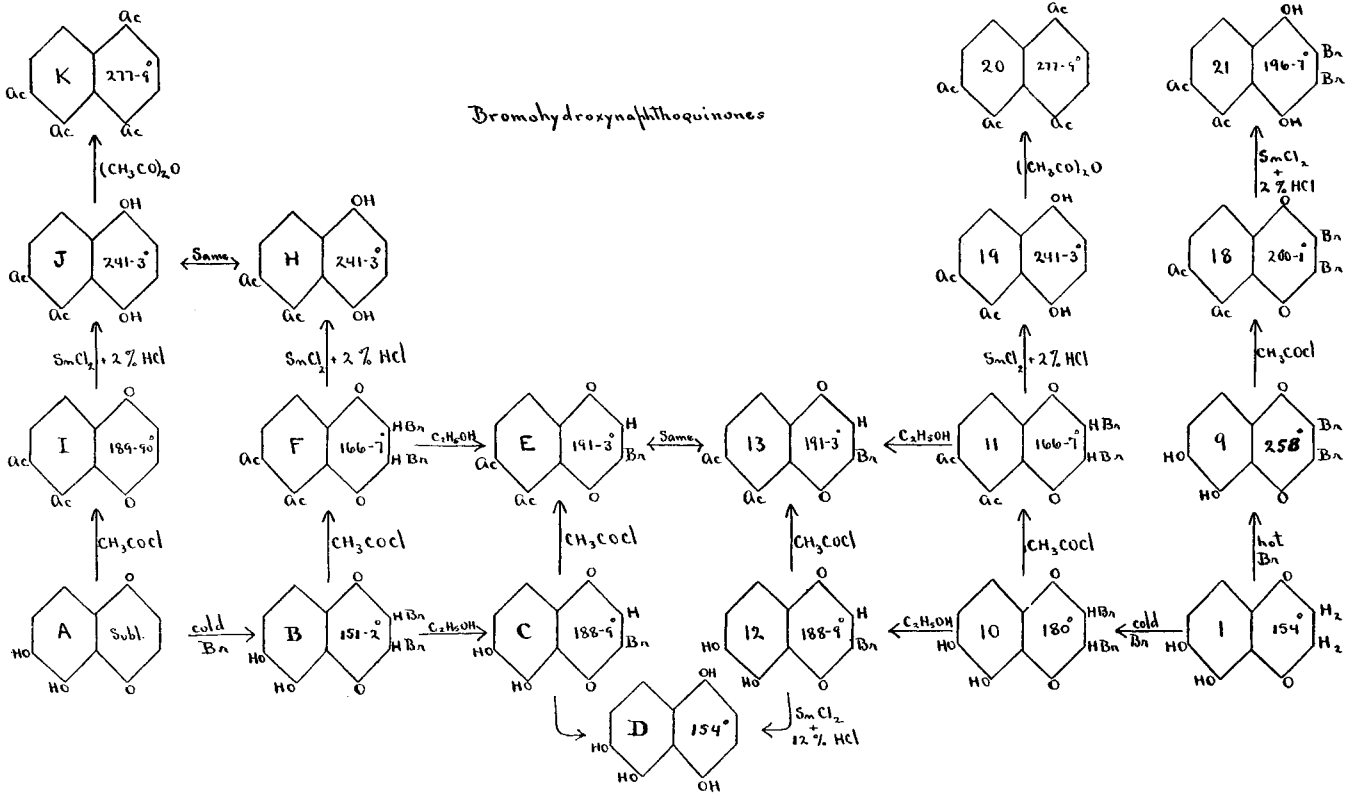
The chart represents the various series of reactions, the derivatives of tetrahydroxynaphthalene being indicated by numbers and those of naphthazarine by letters. The naphthazarine derivatives were prepared with the expectation that they, being identical or similar, would act as checks upon the other series.

By representing the tetrahydroxynaphthalene 1 in the chart as a qui-

[1] This paper forms Part II of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of North Carolina. Part I is found in THIS JOURNAL, **38**, 387 (1916).

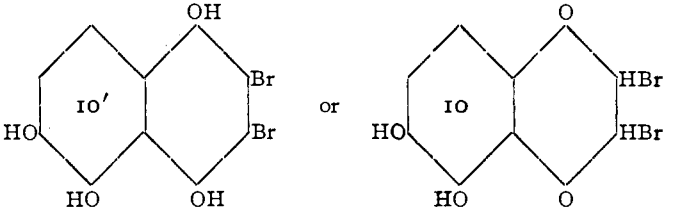
[2] *Ber.*, **47**, 2796 (1914).

[3] V. C. Edwards.


Bromohydroxynaphthoquinones
K 277-9°
J 241-3°
H 241-3°
I 189-90°
F 166-7°
E 191-3°
13 191-3°
11 166-7°
20 277-9°
19 241-3°
21 196-7°
18 200-1°
9 258°
A Subl.
B 151-2°
C 188-9°
D 154°
12 188-9°
10 180°
1 154°
(CH3CO)2O
Same
SnCl2 + 2% HCl
CH3COCl
C2H5OH
cold Bn
hot Bn
SnCl2 + 12% HCl

none, it is more readily understood why the immediate bromination products are quinones. The outstanding puzzle of the investigation presents itself at once. The bromination of 1 with four molecules of bromine in cold glacial acetic acid solution yields the dibromide of a dihydroxyquinone to which we assign the Formula 10. This compound is yellow and melts at 180°. The bromination of naphthazarine with four molecules of bromine in cold chloroform solution yields also the dibromide of a dihydroxyquinone to which we assign Formula B. This compound is yellow but it melts at 151–2°, which is considerably lower than the melting point of 10. A similar constitution was assigned by Zincke and Schmidt[1] to the product of the chlorination of naphthazarine. We found that alcohol, even cold, removes one molecule of hydrobromic acid from the compound B and gives a purple-colored quinone C, containing one atom of bromine. An analogous reaction was obtained by Zincke and Schmidt. Similarly, alcohol removes one molecule of hydrobromic acid from the compound 10, giving the product 12, which is identical with C. Reduction with stannous chloride converts C and 12 into tetrahydroxynaphthalene.

The two possible formulas for the bromination product obtained from 1 are

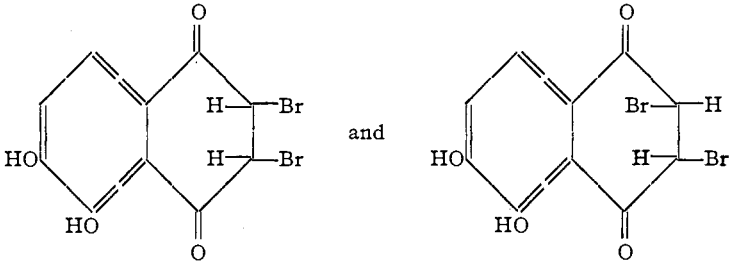


If we adopt 10′, we are at once confronted with the difficulty of removing one molecule of hydrobromic acid by cold alcohol. If a hydrogen atom is removed with an *o*-bromine, then the other hydrogen atom must wander to a meta position. Such a shifting we must regard as impossible. The removal of hydrobromic acid from 10 is a simple matter. There are many analogies for a reaction of that sort. Representing 1 as a quinone, the bromination then is a reaction of simple substitution. The two compounds B and 10 will be designated for the present, α- and β-naphthazarine dibromide.

Our proof of the constitution of 10 goes further in the production of the ring of compounds 10–11–13–12, which involves the identity of 13 with E, a member of the analogous ring B, C, E, F. Compound 10 is converted by acetyl chloride after boiling for sixty hours into a diacetate. Alcohol removes one molecule of hydrobromic acid from this derivative, giving a monobromoquinone, identical with E in the naphthazarine series. Compound 13 was also obtained from 12.

[1] *Ann.*, **286**, 41 (1895).

A New Kind of Isomerism.—So far as we can see there is no escape from the isomerism of the α- and β-naphthazarine dibromides. What sort of an isomerism is it? The suggestion is thrown out that this may be a cis and trans form of isomerism within and without the benzene ring. That is, in one case the two bromine atoms would be outside of the ring and in the other case one would be outside of the ring and the other inside. The formulas then would be



We have no experimental evidence to suggest the nature of the difference. Neither have we been able to convert one form into the other directly.

Bromination in Hot Acetic Acid.—If the bromination of 1 is conducted in hot glacial acetic acid solution, the hydrogen atoms in positions 2,3 are eliminated and the product is a dibromodihydroxyquinone, 9. This compound on boiling one week with acetyl chloride yields a diacetate, 18, which is still yellow. The diacetate on reduction gives the colorless dihydroxydiacetate 21.

In a number of cases the quinones were reduced by stannous chloride to hydroxy compounds. The bromine atoms were eliminated in all cases except in the production of 21 where they are retained.

A third ring of compounds is shown on the chart by formulas A–B–F–H–J–I. The diacetate I is obtained by boiling naphthazarine with acetyl chloride for one week. Zincke and Schmidt used acetic anhydride but this agent too easily produces the tetracetate. The diacetate is reduced by stannous chloride to the dihydroxydiacetate J which is identical with H, obtained from F and also with 19 obtained from 11. Acetylation with acetic anhydride converts J into the tetracetate K which is identical with 20.

Experimental Part.

α-5,6-Dihydroxy-1,4-naphthoquinonedibromide(2,3) or α-Naphthazarinedibromide (B), $C_{10}H_6O_4Br_2$.—Five grams (1 mol) of sublimed naphthazarine were powdered, suspended in 100 cc. of chloroform and treated with 8.4 g. (4 atoms) of bromine. The mixture was mechanically shaken for 4 hrs. when solution was complete. After 8 hrs. yellow crystals began to deposit and in 24 hrs. the reaction was complete. The total yield, after concentrating the mother liquor to about 5 cc., amounted to 6.2 g. The

product was purified by recrystallizing several times from benzene. The dibromide consists of lemon yellow prisms which on heating turn red and then gray from 135° up to 151–2°, where they melt to a dark red liquid with slight decomposition. The crystals are only slightly soluble in ether or ligroin, fairly soluble in chloroform and more readily soluble in alcohol and in benzene.

0.2458 g. gave 0.3104 g. CO_2 and 0.0390 g. H_2O.
0.2180 g. gave 0.2341 g. AgBr.

Calc. for $C_{10}H_6O_4Br_2$: C, 34.30; H, 1.73; Br, 45.68. Found: C, 34.44; H, 1.77; Br, 45.69.

When warmed in alcohol naphthazarine dibromide loses one molecule of hydrobromic acid, becoming monobromonaphthazarine, C. Each of these bromoquinones on reduction with stannous chloride in 12% hydrochloric acid yields tetrahydroxynaphthalene. The dibromide is very slowly acetylated with acetyl chloride.

5,6-Diacetyl-1,4-naphthoquinonedibromide(2,3) or **5,6-Diacetylnaphthazarinedibromide(2,3)** (F), $C_{14}H_{10}O_6Br_2$.—Two grams of naphthazarine dibromide were boiled 60 hrs. with an excess of acetyl chloride in an all glass apparatus. Upon evaporation of the excess of acetyl chloride a mass of colorless plates mixed with some black material remained. The acetate was purified by recrystallizing from carbon tetrachloride. It was found to be soluble in most of the usual organic solvents. The pure product consists of colorless plates which assume a reddish color about 110° and at 166–7° melt to a red liquid. They slowly turn to a deep red color on standing in a desiccator. This change occurs also in the dark and in an atmosphere of nitrogen though more slowly.

0.1478 g. gave 0.2103 g. CO_2 and 0.0314 g. H_2O.
0.1350 g. gave 0.1180 g. AgBr.

Calc. for $C_{14}H_{10}O_4Br_2$: C, 38.71; H, 2.32; Br, 36.83. Found: C, 38.71; H, 2.37; Br, 37.19.

The diacetate when warmed with alcohol loses one molecule of hydrobromic acid, giving the diacetate of monobromonaphthazarine, E. It is reduced by stannous chloride in 2% hydrochloric acid to 1,4-dihydroxy-5,6-diacetylnaphthalene H which is derivable more directly from naphthazarine.

3 (or 2)-Monobromo-5,6-dihydroxy-1,4-naphthoquinone or **3 (or 2)-Monobromonaphthazarine (C)**, $C_{10}H_5O_4Br$.—Naphthazarinedibromide is not stable in alcoholic solution for such a solution soon turns red and beautiful bronze-colored prisms separate out. The preparation of this product was carried out by dissolving 1.6 g. of naphthazarinedibromide in 150 cc. of absolute alcohol and heating under a reflux condenser for 4 hrs. on a water bath. A yield of 0.95 g. was obtained. The product was recrystallized from hot benzene. The crystals are beautiful reddish brown prisms which begin to give off a colored vapor at 170° and melt

at 188–9° to a red liquid. They are difficultly soluble in ether and in alcohol but easily soluble in acetic acid and in benzene.

0.2119 g. gave 0.3473 g. CO_2 and 0.0374 g. H_2O.
0.1630 g. gave 0.1147 g. AgBr.

Calc. for $C_{10}H_5O_4Br$: C, 44.61; H, 1.87; Br, 29.71. Found: C, 44.70; H, 1.97; Br, 29.94.

This compound was also prepared by heating naphthazarinedibromide with an equal weight of sodium acetate in 95% acetic acid. On reduction with stannous chloride in 12% hydrochloric acid it goes over into tetrahydroxynaphthalene. Heated with acetyl chloride it yields the diacetate E which is identical with the diacetate 13.

3 (or 2)-**Monobromo-5,6-diacetyl-1,4-naphthoquinone (E)**, $C_{14}H_9O_6Br$.—One-half gram of the monobromonaphthazarine was heated with excess of acetyl chloride for 60 hrs. On cooling bright yellow crystals deposited, equal in weight to the starting out material. They are best recrystallized from absolute alcohol. When heated they shrink somewhat and melt at 191–2° to a reddish yellow liquid. After resolidification this will melt again at the same point. The product consists of very beautiful silky, yellow needles. Analysis shows a high figure for carbon but no trace of an impurity could be found though much time was spent in a search for it.

0.1418 g. gave 0.2520 g. CO_2 and 0.0350 g. H_2O.
0.1466 g. gave 0.0768 g. AgBr.

Calc. for $C_{14}H_9O_6Br$: C, 47.62; H, 2.53; Br, 22.63. Found: C, 48.46; H, 2.76; Br, 22.25.

This compound is also obtained from dibromodiacetylnaphthazarine, F, by warming with alcohol. When it becomes possible to prepare more of E we will subject it to reduction with stannous chloride in 2% hydrochloric acid.

In view of the series A–B–F–H we regarded it as important to close the ring by preparing the series A–I–J and then subsidiarily the compound K.

5,6-Diacetyl-1,4-naphthoquinone (I).—In preparing this compound Zincke and Schmidt[1] heated naphthazarine with acetic anhydride and sodium acetate. On repeating their work we obtained a product consisting largely of the tetracetate K. We therefore resorted to acetyl chloride.

Four grams of naphthazarine were boiled with acetyl chloride for seven days. The reaction was by no means complete after three days. The product was recrystallized from acetic acid, at first using a little animal charcoal. The golden yellow crystals, melting at 189–90°, were identical with the diacetate of Zincke and Schmidt.

1,4-Dihydroxy-5,6-diacetylnaphthalene (J), $C_{14}H_{16}O_6$.—One-half gram of the diacetylnaphthalene was mixed with excess of stannous chloride and slowly added to 25 cc. of boiling 2% hydrochloric acid. As the yellow quinone dissolved the colorless reduction product crystallized out. After

[1] *Ann.*, **286**, 36 (1895).

five minutes the mixture was cooled and the product filtered off. The yield amounted to 0.4 g. It was recrystallized from much ethyl acetate. The pure substance consists of colorless microscopic rectangular plates which turn red at 230° and melt at 241–3° to a red liquid. It is very soluble in acetone, much less soluble in alcohol or ethyl acetate and insoluble in chloroform and xylene.

0.1498 g. gave 0.3324 g. CO_2 and 0.0584 g. H_2O.
Calc. for $C_{14}H_{16}O_6$: C, 60.85; H, 4.38. Found: C, 60.52; H, 4.36.

Upon heating with acetic anhydride and sodium acetate it is readily converted into tetracetylnaphthalene, K. This melts at 277–9° and is identical with the product obtained by acetylating 1,4,5,6-tetrahydroxynaphthalene.

Bromination of 2,3-Dihydro-5,6-dihydroxy-1,4-naphthoquinone (or 1,4,5,6-Tetrahydroxynaphthalene) at Room Temperature.

β-5,6-Dihydroxy-1,4-naphthoquinonedibromide (2,3) or β-Naphthazarinedibromide (10), $C_{10}H_6O_4Br_2$.—Two grams (1 mol) of the yellow tetrahydroxynaphthalene are dissolved in 50 cc. glacial acetic acid and to this solution at room temperature 6.8 g. (4 mols) bromine are added. The solution assumes a red color and after 3 hrs. lemon-yellow crystals begin to deposit. After 5 hrs. the yield amounts to 2.6 g. and after a day a further yield of 0.3 g. is obtained. The product is soluble in chloroform, alcohol, benzene, and acetic acid. Benzene is the best solvent for purification. The pure substance consists of lemon-yellow prisms which begin to turn red in the vicinity of 140° and melt rather sharply at 180° to a red liquid.

I. 0.2086 g. gave 0.2252 g. AgBr; II. 0.2540 g. gave 0.3200 g. CO_2 and 0.0425 g. H_2O; III. 0.1857 g. gave 0.2345 g. CO_2 and 0.0302 g. H_2O; IV. 0.1594 g. gave 0.2010 g. CO_2 and 0.0266 g. H_2O; V. 0.1766 g. gave 0.1898 g. AgBr.

	C.	H.	Br.
Calc. for $C_{10}H_6O_4Br_2$:	34.30	1.73	45.68
Found: I.	....	...	45.93
II.	34.35	1.86	....
III.	34.43	1.82	....
IV.	34.49	1.86	....
V.	....	...	45.73

The dibromide loses hydrobromic acid in the sunlight and is changed to a steel blue substance which we have not especially studied. One molecule of hydrobromic acid is readily removed by alcohol, giving the compound 12, which is identical with monobromonaphthazarine, C. Both 12 and C are reduced and debrominated by stannous chloride in 12% hydrochloric acid, going back to tetrahydroxynaphthalene, D. The dibromide 10 when boiled one week with acetyl chloride yields the diacetate 11, melting at 166–7°, which is identical with F. This identification was made more certain by the following analysis:

0.1670 g. gave 0.2368 g. CO_2 and 0.0361 g. H_2O.
Calc. for $C_{14}H_{10}O_6Br$: C, 38.71; H, 2.32. Found: C, 38.67; H, 2.42.

This diacetate 11 is also deprived of hydrobromic acid by alcohol, giving the monobromo-diacetate 13, which is identical with E. The preparation of 13 in this way enabled us to close another ring, 10–11–13–12, by acetylating 12 with acetyl chloride, thus preparing 13 by another method.

Another reaction of the diacetate 11 is its reduction with stannous chloride in 2% hydrochloric acid to the colorless compound 19, which is identical with J described above. This diacetate 19 was acetylated with acetic anhydride and sodium acetate, giving the completely acetylated product the tetracetate 20, which is identical with K.

If the dibromide 10 is boiled with glacial acetic acid, the solution turns red and red leaf-like crystals soon deposit. These crystals melt at 200–38° with partial sublimation. Analyses failed to indicate a pure product. A bromine determination, however, suggested an isomeric form of the diacetate 11.

Bromination of 2,3-Dihydro-5,6-dihydroxy-1,4-naphthoquinone (or 1,4,5,6-Tetrahydroxynaphthalene) in Hot Acetic Acid.

2,3-Dibromo-5,6-dihydroxy-1,4-naphthoquinone or 2,3-Dibromonaphthazarine (9), $C_{10}H_4O_4Br_2$.—Two grams (1 mol) of tetrahydroxynaphthalene are dissolved in 50 cc. of hot glacial acetic acid and 6.8 g. (4 mols) of bromine are added. The flask is suspended over a water both so that the temperature is held at about 70°. Red crystals soon begin to deposit in the hot solution. After 4 hrs. the reaction is complete and a yield of 2.7 g. is obtained. Acetic acid is the best solvent for purification. The pure substance consists of red leaves which begin to give off a colored vapor at 230° and melt at 258°. It is slightly soluble in alcohol and in ether.

I. 0.2054 g. gave 0.2600 g. CO_2 and 0.0270 g. H_2O; II. 0.2090 g. gave 0.2668 g. CO_2 and 0.0254 g. H_2O; III. 0.1938 g. gave 0.2100 g. AgBr; IV. 0.1538 g. gave 0.1665 g. AgBr.

	C.	H.	Br.
Calc. for $C_{10}H_4O_4Br_2$:	34.49	1.15	45.94
Found: I	34.51	1.47	....
II	34.81	1.36	....
III	....	...	46.10
IV	....	...	46.06

When it becomes possible to prepare more material, this compound will be reduced with stannous chloride. Its acetylation is described below.

2,3-Dibromo-5,6-diacetyl-1,4-naphthoquinone (18), $C_{14}H_8O_6Br_2$.—Two grams of dibromonaphthazarine 9 were heated one week with acetyl chloride in an all glass apparatus. The solution gradually turned yellow and then yellow crystals began to deposit. Before filtering off the product, the solution was concentrated to a small bulk. After recrystallizing from

acetic anhydride the product weighed 2.3 g. The pure substance is easily soluble in hot acetic anhydride, alcohol and carbon tetrachloride, crystallizing in each case in beautiful yellow needles. The substance melts at 200–1°.

0.1998 g. gave 0.2850 g. CO_2 and 0.0358 g. H_2O.
0.1048 g. gave 0.0915 g. AgBr.

Calc. for $C_{14}H_8O_6Br_2$: C, 38.89; H, 1.87; Br, 37.01. Found: C, 38.89; H, 1.97; Br, 37.15.

The bromine is not removed by stannous chloride in 2% hydrochloric acid as shown below.

1,4-Dihydroxy-2,3-dibromo-5,6-diacetylnaphthalene (21), $C_{10}H_{14}O_6Br_2$. —One-half gram of dibromodiacetylnaphthazarine is suspended in 15 cc. of 2% hydrochloric acid and about 5 g. of stannous chloride are added. The mixture is heated and as the yellow naphthazarine passes into solution, colorless crystals separate out. The yield amounts to a half gram. The product is insoluble in benzene and ligroin but is soluble in hot amyl alcohol, chloroform and ethyl acetate. It is best recrystallized from a large volume of hot chloroform. The pure substance consists of small colorless needles which melt to a red liquid at 196–7°.

0.1263 g. gave 0.1772 g. CO_2 and 0.0286 g. H_2O.

Calc. for $C_{14}H_{10}O_6Br_2$: C, 38.71; H, 2.32. Found: C, 38.26; H, 2.53.

This compound is isomeric with 11 but it is not a quinone. It is the only product obtained in our work which has retained its bromine after stannous chloride treatment.

CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY, AND THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE.]

THE REDUCTION OF 4-ANISALHYDANTOIN 1-ACETIC ACID AND ITS ETHYL ESTER.

BY DOROTHY A. HAHN AND C. PAULINE BURT.
(In coöperation with TREAT B. JOHNSON.)
Received August 23, 1917.

In a previous paper from the Sheffield Laboratory[1] the fact was noted that in the reduction of 4-anisalhydantoin 1-acetic acid by means of zinc in acetic acid and by means of sodium amalgam in alcoholic solution (kept neutral by additions of acetic acid) products were encountered which showed no tendency to melt at 315° and which were convertible into the original acid. It was not possible at the time to obtain pure substances and to clear the matter up. The evidence, however, seemed to point to the possibility that we were dealing here with geometrical isomerides.

These reactions have since been made the subject of further investigation, and it has been found that in both cases of reduction salts are formed as intermediate products in the course of the reaction.

[1] Johnson and Hahn, THIS JOURNAL, **39**, 1263 (1917).