

ether gave on sublimation colorless needles of a product (m. p. 130–131°) which was identified as phthalic anhydride by mixed melting point determination.

**With 4-Benzyl-1,2-naphthoquinone.**—A solution of 1 g. of the quinone in 20 cc. of acetic anhydride containing one drop of concentrated sulfuric acid was heated for one hour on the steam-bath, and then clarified with Norite and poured into water. The precipitated material, crystallized from methanol, formed colorless prisms, m. p. 139.5–140°, corr.; yield, 0.8 g. The compound depresses the melting point of 1,2,4-triacetoxynaphthalene (m. p. 135°).

*Anal.* Calcd. for  $C_{23}H_{20}O_6$ : C, 70.37; H, 5.14. Found: C, 70.41; H, 5.09.

The same compound was obtained by heating the quinone with acetic anhydride and sodium acetate for one hour on the steam-bath.

**3-Chloro-1,2,4-triacetoxynaphthalene** was obtained by heating 3-chloro-1,2-naphthoquinone (1 g.) with acetic anhydride (10 cc.)–sulfuric acid (2 drops) on the steam-bath for three hours and crystallizing the product from alcohol (yield, 0.85 g.). It forms colorless microcrystals, m. p. 172–173°.

*Anal.* Calcd. for  $C_{16}H_{13}O_6Cl$ : C, 57.04; H, 3.89. Found: C, 57.03; H, 4.14.

Treated in the same way, 4-chloro-1,2-naphthoquinone was recovered unchanged.

## Summary

4-Methyl- and 4-benzyl-1,2-naphthoquinone have been synthesized and the former substance has been converted into a derivative obtainable by the degradation of the known 4-dicarbethoxymethyl-1,2-naphthoquinone.

The 4-methyl, 4-benzyl, and 4-dicarbethoxymethyl compounds all react with aniline with displacement of the 4-alkyl group. The first two compounds unexpectedly react with acetic anhydride–sulfuric acid to give colorless triacetates. The benzyl and malonic ester derivatives slowly add 2,3-dimethylbutadiene.

The three alkyl derivatives all have properties characteristic of true quinones, and the dicarbethoxymethyl compound is capable also of reacting in the tautomeric form to give an acetate. A substance described in the literature as the acidic tautomer of 4-methyl-1,2-naphthoquinone is believed to have some other structure.

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## The Dissociation of Hydantoin

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In a recent paper, Zief and Edsall<sup>1</sup> have shown that hydantoin and 5,5'-dimethylhydantoin have nearly equal dissociation constants, and have pointed out that the ionizing hydrogens are thus shown to be from the imino rather than the methylene group in hydantoin. The results of a series of electrometric titrations which are presented here not only confirm this conclusion, but also show from which nitrogen the dissociation occurs and to what extent dissociation is affected by the presence of various other substituents in the hydantoin molecule. The results of this study support the observations of the chemical behavior of these same compounds as reported by Hahn and co-workers.<sup>2</sup>

### Experimental

**Compounds.**—The substances used were purified analyzed samples of compounds whose preparation has been described<sup>2</sup> and were kindly supplied by Dr. Hahn. Their structural formulas and melting points are given in Table I

(1) Zief and Edsall, *THIS JOURNAL*, **59**, 2245 (1937).

(2) Hahn and Evans, *ibid.*, **50**, 806 (1928); Hahn and Litzinger, *ibid.*, **54**, 4663 (1932); Litzinger, *ibid.*, **56**, 673 (1934); Hahn and Seikel, *ibid.*, **58**, 647 (1936); unpublished work.

together with numbers by which they will be designated in the paper.

**Methods.**—The cell used in most of the measurements consisted of a hydrogen and a saturated calomel electrode which were frequently checked by measuring the *pH* of 0.1 *N* hydrochloric acid. The potential of the calomel electrode was taken as 0.2473 v. at 25°. Measurements were made with a Leeds and Northrup simplified potentiometer and galvanometer no. 2420.

In one typical series of experiments, samples weighing 0.4142 m. e. were dissolved in 25 ml. of water which had been freed from carbon dioxide. In most cases it was necessary to heat to 50° in order to effect complete solution, after which the solutions were cooled in an atmosphere of hydrogen and titrated at constant temperature with carbonate-free potassium hydroxide (0.04467 *N*) using a microburet.

A glass electrode was used for some determinations in order to check the results obtained with the hydrogen electrode and thus be certain that the substances used were not reduced at the hydrogen electrode. The results by the two methods agreed.

In addition to the titrations, the *pH*'s of solutions containing an equal number of equivalents of acid and of salt were measured in each case. These solutions were made by dissolving a weighed quantity of the sample in a measured volume of standard base. Concentrations varying from 0.05 to 0.005 *N* were used in some cases in

No.	Name	TABLE I Formula	M. p., °C.	pH	pK'	pK <sub>1</sub>
I	Hydantoin	$\text{NHCONHCOCH}_2$	220	9.12	9.12 <sup>a</sup>	
II	Benzylhydantoin	$\text{NHCONHCOCH}_2\text{CH}_2\text{C}_6\text{H}_5$	86-87	9.03	9.03	
III	N-3-Methyl-5-benzylhydantoin	$\text{NHCON}(\text{CH}_3)\text{COCH}_2\text{CH}_2\text{C}_6\text{H}_5$	140-141		(>14)	
IV	Benzylhydantoin-N-1-acetic acid	$\text{N}(\text{CH}_2\text{COOH})\text{CONHCOCH}_2\text{CH}_2\text{C}_6\text{H}_5$	110-111		2.81	8.96
V	Hydantoin-N-1-phenylpropionic acid	$\text{N}(\text{CH}(\text{CH}_2\text{C}_6\text{H}_5)\text{COOH})\text{CONHCOCH}_2$	157-158		2.91	9.21
VI	N-3-Methyl-5-benzylhydantoin-N-1-acetic acid	$\text{N}(\text{CH}_2\text{COOH})\text{CON}(\text{CH}_3)\text{COCH}_2\text{CH}_2\text{C}_6\text{H}_5$	149.5-150.5	3.22	3.16	
VII	Methyl 5-benzylhydantoin-N-1-acetate	$\text{N}(\text{CH}_2\text{COOCH}_3)\text{CONHCOCH}_2\text{CH}_2\text{C}_6\text{H}_5$	118-120	7.81	7.81 <sup>b</sup>	
VIII	N-1-Methyl 5-benzylhydantoin-N-3-acetic acid	$\text{N}(\text{CH}_3)\text{CON}(\text{CH}_2\text{COOH})\text{COCH}_2\text{CH}_2\text{C}_6\text{H}_5$	136.5-137.5	3.12	3.05	
IX	Benzalhydantoin	$\text{NHCONHCOC}=\text{CHC}_6\text{H}_5$	220		8.6 <sup>c</sup>	
X	N-3-Methyl-5-benzalhydantoin	$\text{NHCON}(\text{CH}_3)\text{COC}=\text{CHC}_6\text{H}_5$	220-221		9.6 <sup>c</sup>	
XI	N-1,N-3-Dimethyl-5-benzalhydantoin	$\text{N}(\text{CH}_3)\text{CON}(\text{CH}_3)\text{COC}=\text{CHC}_6\text{H}_5$	85-86		(>14) <sup>c</sup>	

<sup>a</sup> Value reported by Edsall 9.12. <sup>b</sup> The low value may be caused by the partial hydrolysis of the ester. <sup>c</sup> These values were estimated from titrations in 95% alcohol.

order to determine the effect of varying ionic strength. The water used in these experiments was distilled three times, the second time from alkaline permanganate.

Since benzalhydantoin and its methyl derivative are extremely insoluble in water, measurements of these compounds were made in 95% alcohol solution. For pur-

acidic with dissociation constants of nearly the same magnitude, the former being slightly smaller. If, however, a methyl group is substituted in the N-3 position of benzylhydantoin, the immediate rise in the pH of the solution when a few drops of base are added shows that there is no detectable evidence of a dissociating hydrogen. Thus the N-1 hydrogen in this compound has no tendency to dissociate (or, at least, a tendency no greater than that of water) and the slight acidity of hydantoin and benzylhydantoin must be attributed solely to the hydrogen in the N-3 position.

The same conclusion is apparent from a comparison of acids IV and VI also shown in Fig. 1. These acids are alike except for the fact that VI has a methyl group substituted for hydrogen in the N-3 position. The latter is seen to be a monobasic acid with a sharply defined end-point while IV shows definitely the existence of two end-points, the second of which must represent the complete dissociation of the N-3 hydrogen.

The comparison of benzalhydantoin and its N-3 methyl derivative with benzylhydantoin and the corresponding methylbenzylhydantoin was thought to be of interest in showing the effect

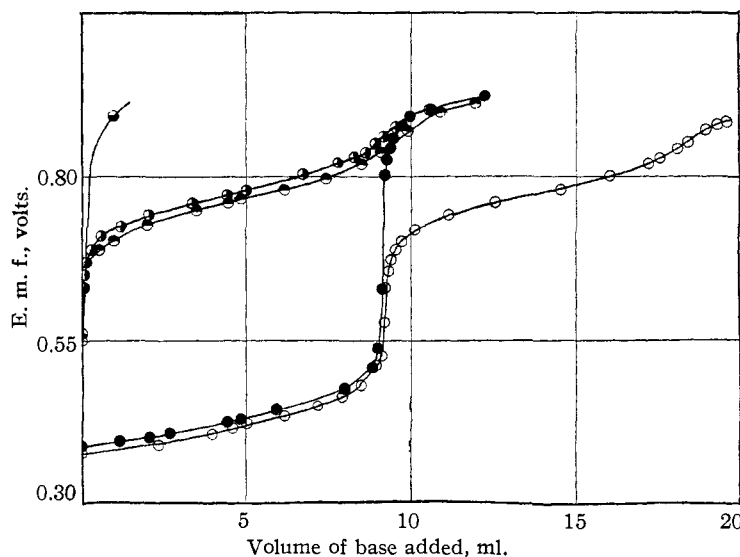


Fig. 1.—Electrometric titration curves of hydantoin derivatives to show contrast between compounds with hydrogen or with a methyl group in the N-3 position (II vs. III) (IV vs. VI). ○, I; ●, II; ●, III; ○, IV; ●, VI.

poses of comparison hydantoin and benzylhydantoin were titrated both in aqueous and alcoholic solutions.

### Results

The titration curves in Fig. 1 show that hydantoin and benzylhydantoin are very weakly

of the double bond in the 5-position on the ionization. These measurements could not be made in aqueous solution because of the insolubility of the benzalhydantoin and could only be carried out in 95% alcohol. Even so, the hydantoin was not wholly in solution at the beginning of the titration but it had dissolved completely in each case before the half equivalent point was reached. Edsall and Blanchard<sup>3</sup> have discussed the fact that if  $x$  and  $y$  are two compounds of an homologous series containing the same dissociating group, the ratio  $K_y/K_x$  will be approximately independent of the solvent. A similar relation for hydantoin and benzylhydantoin in alcohol and water was found to hold approximately. Hence it was felt that a comparison of the titration curves of benzal- and benzylhydantoin should have at least qualitative significance. Figure 2 shows that benzalhydantoin is slightly more acidic than benzylhydantoin and that N-3-methylbenzalhydantoin has a small but measurable dissociation constant in contrast to N-3-methylbenzylhydantoin. Chemical observations support the fact that the N-1 hydrogen in the unsaturated compound has a salt-forming tendency.

In Table III are listed values of  $pH$  for solutions in which there were equivalent quantities of salt and unneutralized acid measured at 22°. These represent the values of  $pK$  as a first approximation. The values of the apparent dissociation constant,  $pK'$ , calculated according to Zief and Edsall<sup>1</sup> are also given for purposes of comparison. Since these values were calculated for solutions whose ionic strength was 0.01 the values of  $pK$  at infinite dilution would be ex-

pected to be larger by  $0.5\sqrt{\mu}$  or 0.05 unit. The values of  $pK_1$  and  $pK_2$  for the dibasic acids were calculated from the titration data according to Britton<sup>4</sup> and do not include corrections for the ionic strength.

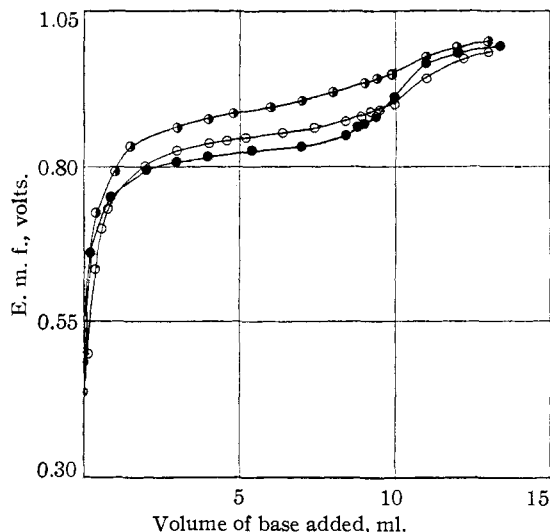


Fig. 2.—Electrometric titration curves of hydantoin, benzalhydantoin and its N-3 methyl derivative in 95% alcohol solution to show evidence of slight dissociation of latter: ○, hydantoin I; ●, benzalhydantoin IX; ●, N-3-methyl-benzalhydantoin X.

### Summary

Electrometric titration curves or dissociation constants of hydantoin and ten related compounds are presented. These show that in the saturated compounds only the N-3 hydrogen dissociates, but that in benzalhydantoin there is a small but measurable dissociation of the N-1 hydrogen.

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(3) Edsall and Blanchard, *THIS JOURNAL*, **56**, 2337 (1933).

(4) Britton, *J. Chem. Soc.*, **127**, 1896 (1925).