Compound I was prepared in a manner similar to that described above. For its properties, see Table I.

3,4-Dihydro-3-phenyl-1,3,2H-benzoxazine (IV). To a solution of 2.5 g. of *N*-(2-hydroxybenzyl)aniline in 25 ml. of methanol, 2 ml. of 37% formaldehyde solution was added. The mixture was heated on a water bath under reflux for 2 hr. The solvent was removed by distillation *in vacuo* and the residue was allowed to stand for 3 days. The product was recrystallized from warm methanol resulting in white needle crystals, yield 57.0%, m.p. 55.9°, readily soluble in acetone and ether, soluble in chloroform, alcohol, and benzene, slightly soluble in ligroin, insoluble in water.

Compounds III, V, VI, and VII were prepared in a manner similar to that described above. For their properties, see Table II.

N,N-Bis(2-hydroxybenzyl)-p-bromoaniline (VIII). Two different procedures for the preparation of this compound are given below.

Procedure A. To a solution of 2.5 g. of saligenin[10] (0.02 mole) in 2.0 ml. of ethanol, 2.8 g. of *N*-(2-hydroxybenzyl)-*p*-bromoaniline (0.01 mole) was added. After heating on a water bath for 12 hr. under reflux, the reaction mixture was cooled in an ice bath and a crystalline substance was obtained. The product was recrystallized from ethanol yielding white leaflets; yield 40.0%, m.p. 156.4°, readily soluble in acetone and ether, soluble in chloroform and alcohol, slightly soluble in ligroin, insoluble in water.

Compounds IX, X, and XI were prepared in a manner similar to that described above. For their properties, see Table III.

Procedure B. A mixture consisting of 103 g. of *p*-bromoaniline (0.6 mole), 49.6 g. of saligenin (0.4 mole) and 200 ml. of ethanol containing 0.6 g. of potassium hydroxide was heated on a water bath under reflux for 14 hr. After being allowed to cool to room temperature, the reaction mixture was neutralized with acetic acid. Unreacted *p*-bromoaniline was removed by steam distillation. The resulting brown, resinous substance was washed several times by being poured into hot water and allowed to cool. The thus formed crystals were recrystallized from methanol-water (1:1) until a constant melting point was attained, white leaflet crystals of *N*-(2-hydroxybenzyl)-*p*-bromoaniline (m.p. 125.3°, yield 36.0%) were separated.

The residue was treated with methanol-water (1:1) until a constant m.p. was obtained yielding white granular crystals; m.p. 156.4°, yield 5%. The melting point of this product was not depressed by admixture with the product prepared by procedure A.

Compounds X and XI were prepared in a manner similar to that described above.

Acknowledgment. I wish to thank Prof. M. Imoto of the Osaka City University for his encouragement throughout this work. I am also grateful to the Matsushita Electric Works, Ltd., Technical Research Department, and indebted to Mr. S. Nagase for much technical assistance.

OSAKA PREFECTURE, JAPAN

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[10] S. Seto and H. Horiuchi, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **57**, 689 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Mechanism of the Tungstic Acid Catalyzed Hydroxylation of Olefins

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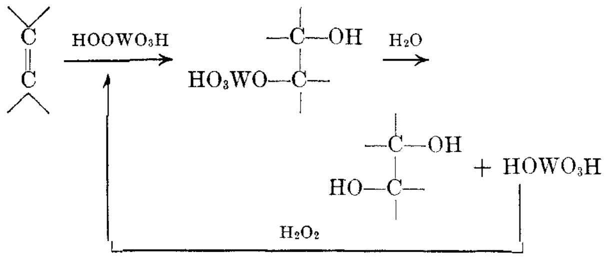
Received February 9, 1959

The electrophilic nature of the tungstic acid catalyzed *trans*- addition of hydrogen peroxide to an olefin has been demonstrated. One of the oxygens introduced by the tungstic acid catalyzed hydroxylation has been shown to arise from the oxidizing agent, the other from the solvent medium. These results are discussed in terms of the mechanism of the reaction, which apparently is analogous to that proposed for organic acid hydroxylations.

Since the first description[2] of tungstic acid as an effective catalyst for the addition of hydrogen peroxide to an ethylenic linkage to give a high yield of the corresponding vicinal glycol, the method has received only sporadic attention.[3,4] Mugdan and Young[3] have suggested that the hydroxylation reaction involves and ionic 1,2-*trans*-addition of an intermediate peroxy acid, $HOOWO_3H$,[5] to the double bond since in all cases thus far reported the addition of the two hydroxyl groups proceeds in the *trans*-direction. The following mechanism has been proposed.[3]



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[1] Present address: Elastomer Chemicals Department, Research Division, E. I. du Pont de Nemours and Co., Wilmington 98, Del.

[2] I. Bergsteinsson, U. S. Patent **2,373,942** (April 17, 1945).

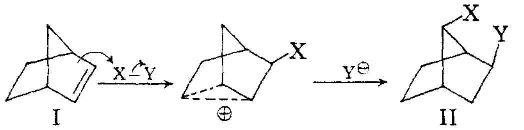
[3] M. Mugdan and D. P. Young, *J. Chem. Soc.*, 2988 (1949).

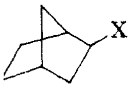
[4] J. M. Church and R. Blumberg, *Ind. Eng. Chem.*, **43**, 1780 (1951); D. P. Young, Brit. Patent **654,764** [*Chem. Abstr.*, **46**, 7115 (1952)]; L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 4041 (1952); C. W. Smith, U. S. Patent **2,838,575** (June 10, 1958).

[5] Potentiometric and calorimetric measurements have established that a faint yellow solution of pertungstic acid results when tungsten trioxide was dissolved in aqueous hydrogen peroxide. A. Lottermoser, *Z. Electrochem.*, **35**, 610 (1929); F. Rivenq, *Bull. soc. chim. France*, **12**, 283 (1945).

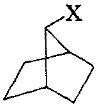
The objective of the present work has been to gain further evidence for the ionic character of the tungstic acid catalyzed addition reaction and also to determine the extent of oxygen transfer from the oxidizing agent to the olefin.

In this connection an examination of the tungstic acid reaction with bicyclo[2.2.1]hept-2-ene (I) was undertaken. This ring system is of particular interest for the elucidation of an ionic addition process, since Wagner-Meerwein rearrangements are a familiar feature of the bicyclo[2.2.1]heptyl cations. For example, rearrangements have been observed in the additions of bromine,[6] hypochlorous acid,[7] and organic peracids[8] to norbornene (I). In each case the predominant reaction product (II) was the result of a Wagner-Meerwein rearrangement. The analogous structural changes have not been observed in the corresponding bicyclo[2.2.1]heptyl free radicals. The bicyclic radicals[9] generated in chain additions to norbornene (I) give as major products the unrearranged material III. In no case has a rearranged 7-substituted norbornane (IV) been isolated.





III



IV

Bicyclo[2.2.1]hept-2-ene (I) was allowed to react with a solution of hydrogen peroxide in *t*-butyl alcohol containing a catalytic amount of tungstic acid to yield a viscous oil. Acetylation of the oil gave *exo-syn*-2,7-diacetoxybicyclo[2.2.1]heptane in an over-all yield of 57%. Lithium aluminum hydride reduction of the 2,7-diacetate afforded the known *exo-syn*-bicyclo[2.2.1]heptane-2,7-diol in a 76% yield, identical in all respects with an authentic sample.

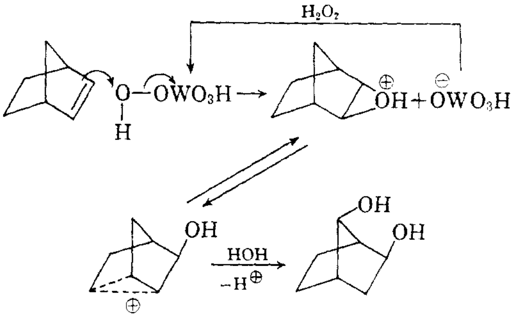
Since rearrangement of the bicycloheptyl ring system has been observed in the tungstic acid catalyzed hydroxylation of norbornene (I), the cationic nature of the addition reaction has been established.

It was also of interest to determine the extent of oxygen transfer from the oxidizing agent to the olefin. Since it has been shown that the rate of exchange between hydrogen peroxide and water is almost negligible[10] and tungstic acid is a powerful hydroxylation catalyst in an aqueous solution,[2,3] particularly convenient experimental conditions could be employed. Crotyl alcohol was allowed to react with tungstic acid dissolved in a 2*M* hydrogen peroxide-water-O^{18} solution. The O^{18} content of the solvent was determined by an equilibration with carbon dioxide and was found to have an enrichment of 1.26% excess O^{18}. The butane-1,2,3-triol contained 1.19% excess of O^{18}. It is clear from these data that the tungstic acid catalyzed hydroxylation involves the introduction of one of the hydroxyl groups from the hydrogen peroxide and the other arises from the solvent.

Since the completion of this work tungstic acid catalyzed reactions of cyclohexene with 90% hydrogen peroxide in methanol, ethanol, and 2-propanol have been reported[11] to yield the corresponding 2-alkoxycyclohexanols, a result which is in agreement with the above O^{18} transfer experiment.

Recently[12] it has been disclosed that hydrogen peroxide catalyzed by sodium tungstate in a near neutral aqueous solution is an effective reagent for the preparation of epoxides.

Thus it becomes apparent from the information which has now been accumulated that the mechanism of the tungstic acid catalyzed hydroxylation of an unsaturated linkage is directly analogous to that proposed for organic peracids.[13]



EXPERIMENTAL[14]

exo-syn-Bicyclo[2.2.1]heptane-2,7-diol. A. Performic acid method. The performic acid hydroxylation of bicyclo[2.2.1]-

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(6) H. Kwart and L. Kaplan, *J. Am. Chem. Soc.*, **76**, 4072 (1954).

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(11) G. B. Payne and C. W. Smith, *J. Org. Chem.*, **22**, 1682 (1957); C. W. Smith, D. G. Norton, and G. B. Payne, U. S. Patent **2,808,442**.

(12) J. R. Skinner, C. H. Wilcoxen, Jr., and G. J. Carlson, U. S. Patents **2,833,787** and **2,833,788** (May 6, 1958); G. B. Payne and P. H. Williams, *J. Org. Chem.*, **24**, 54 (1959).

(13) D. Swern, *Org. Reactions*, VII, 378 (1957).

(14) Oxygen-18 analyses were performed using the method of W. E. von Doering and E. Dorfman, *J. Am. Chem. Soc.*, **75**, 5595 (1953). Microanalyses were performed by B. J. Nist and C. H. Ludwig of this department. Melting points are corrected and boiling points are uncorrected.

2-heptene was conducted in the previously described manner[8] to give a 74% yield of pure *exo-syn*-bicyclo[2.2.1]-heptane-2,7-diol, m.p. 172–174° (sealed tube), reported[8] m.p. 174–176°. The infrared spectrum (chloroform solution) exhibited a strong 3.03 μ hydrogen-bonded hydroxyl band.

Diacetate. Treatment of the 2,7-diol with acetic anhydride in pyridine gave a colorless diacetate, b.p. 129–131° at 10 mm., $n_D^{23.5}$ 1.4629.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.3; H, 7.6. Found: C, 62.1; H, 7.5.

Dibenzoate, m.p. 106–107° (ether-hexane).

Anal. Calcd. for $C_{21}H_{20}O_4$: C, 75.0; H, 6.0. Found: C, 74.9; H, 5.8.

B. Tungstic acid catalyzed hydroxylation. To 10 ml. (0.066 mole) of a 6.6*M* solution of hydrogen peroxide in *t*-butyl alcohol, prepared by dilution of 90% hydrogen peroxide with the alcohol, was added 100 mg. of tungstic acid. The faint yellow mixture was stirred until the catalyst dissolved. The pertungstic acid solution was diluted with 22 ml. of *t*-butyl alcohol and 4.71 g. (0.05 mole) of bicyclo-[2.2.1]-2-heptene was added. The homogeneous reaction mixture was heated, with stirring, at 70° in an oil bath. After a few minutes an exothermic reaction ensued which was allowed to subside before heating at 70° was continued. After a total reaction time of 3 hr. at 70°, approximately 90% of the peroxide had been consumed and no further uptake was noted. The reaction mixture was allowed to cool, filtered to remove a small amount of insoluble material, and the solvent was evaporated. The residual oil was treated with 40 ml. of acetic anhydride and one drop of concentrated sulfuric acid. An exothermic reaction followed and the solution was allowed to stand at room temperature for 3 hr. A small amount of calcium carbonate was added to neutralize the catalyst, the mixture was shaken, filtered, and concentrated at 40–50° under reduced pressure. The residue was diluted with 200 ml. of water and the oily layer extracted with three 100-ml. portions of ether. The combined ether extracts were washed with 50 ml. of 10% sodium bicarbonate solution, 200 ml. of water, and then dried over anhydrous magnesium sulfate. Distillation gave 6.02 g. (57%) of *exo-syn*-2,7-diacetoxybicyclo[2.2.1]heptane, b.p. 130–134° at 11 mm., n_D^{25} 1.4620. The infrared spectrum (Neat) was identical with that of an authentic sample. Lithium aluminum hydride reduction of the 2,7-diacetate gave a 76% yield of *exo-syn*-bicyclo[2.2.1]heptane-2,7-diol, m.p. 174–176°, undepressed on admixture with the diol obtained from the performic acid oxidation. The dibenzoate, m.p. 105.5–106.5°, was identical in all respects with an authentic sample.

Tungstic acid catalyzed hydroxylation of crotyl alcohol in oxygen-18 enriched water. A solution of 1.5 ml. of a 35.5*M* aqueous solution of hydrogen peroxide and 20 ml. of enriched water containing approximately 1.3% excess of oxygen-18[15] was equilibrated by shaking with ordinary carbon dioxide for 5 hr. Mass spectrometric analysis of the resultant carbon dioxide indicated that the solvent contained 1.30% excess of oxygen-18. To the hydrogen peroxide-water-O^{18} solution was added 50 mg. of tungstic acid and 3.61 g. (0.05 mole) of crotyl alcohol (b.p. 120–121°). After an initial exothermic reaction the solution was heated at 70° for 2 hr., after which most of the peroxide had been consumed. The reaction mixture was cooled and equilibrated with ordinary carbon dioxide. Analysis of the carbon dioxide indicated that the solvent contained 1.23% excess of O^{18}. Distillation gave 3.9 g. (74%) of butane-1,2,3-triol-O^{18}, b.p. 155–156° at 11 mm.,[16] n_D^{25} 1.4614, containing 1.19 ± 0.01% excess of oxygen-18.

SEATTLE 5, WASH.

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[15] Obtained from the Stuart Oxygen Co. on allocation from the Atomic Energy Commission.

[16] Reported b.p. 170° at 20 mm., n_D^{20} 1.4622, ref. 3.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF URSINUS COLLEGE AND THE RESEARCH LABORATORIES OF MAUMEE CHEMICAL CO.]

Isatoic Anhydride. IV. Reactions with Various Nucleophiles

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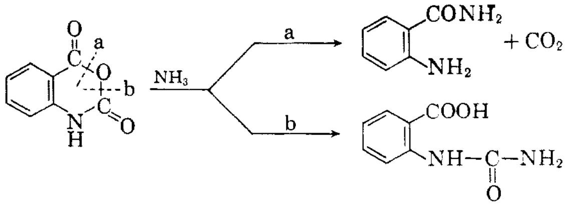
The reactions of isatoic anhydride have been extended to include alcohols, mercaptans, and compounds with active methylene groups forming substituted esters, thio esters, carbamates, and substituted quinolines. A mechanism for the alternate cleavage of the anhydride ring is elucidated.

Reactions of isatoic anhydride (IA) with ammonia, primary and secondary amines, and amides have previously been studied.[2–4] In the latter two references it was reported that the reaction with ammonia followed two competing paths, producing either anthranilamide or *o*-ureidobenzoic acid, or their substituted derivatives with amines. At that time no speculation was made relating the two observed alternate types of cleavage of the anhydride ring:



The present investigators have found that in addition to the amines previously reported, isatoic anhydride reacts readily with the following nucleophilic reagents: primary and secondary alcohols, phenols, thiophenols, mercaptans, and ethyl

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[1] (a) Department of Chemistry, Ursinus College, Collegeville, Pa. (b) Maumee Chemical Company, Toledo 5, Ohio.

[2] R. H. Clark, *J. Org. Chem.*, **9**, 55 (1944).

[3] R. P. Staiger and E. C. Wagner, *J. Org. Chem.*, **13**, 347 (1948).

[4] R. P. Staiger and E. C. Wagner, *J. Org. Chem.*, **18**, 1427 (1953).