*Anal.* Calcd. for base·$2HAuCl_4·5H_2O$: Au, 38.72. Found: Au, 38.71.

Nonalupine picrate recrystallized from 50% alcohol melted at 185–186°.

**Oxidation of Nonalupine.**—Nonalupine (5 g.) in 600 cc. of water was treated with a saturated solution of potassium permanganate in the cold until the pink color persisted for twenty-four hours. The filtrate was extracted with chloroform, which took out an oil (2.5 g.) that slowly crystallized. Recrystallized from a mixture of chloroform and petroleum ether the substance formed long flat crystals, m. p. 168.5–170.5°. On drying in the oven it slowly volatilized, losing 28% of its weight in fifteen days at 110°. A further crop (2 g.) of the substance was obtained by extracting the precipitated manganese dioxide with alcohol.

*Anal.* Calcd. for $C_{15}H_{24}O_3N_2$: C, 64.24; H, 8.63; N, 9.99. Found: C, 63.99, 64.18; H, 8.45, 8.58; N, 9.84, 9.94.

The substance was recovered unchanged after warming with sulfur dioxide in water. It is readily soluble in water and the solution is neutral to test papers.

**Oxynonalupine Gold Chloride.**—This compound is quite soluble in water. On slow evaporation it forms small yellow needles, m. p. 238–239°. Analysis indicated a partial reduction of the base on combination with gold chloride.

*Anal.* Calcd. for $C_{16}H_{24}O_2N_2·HAuCl_4$: Au, 32.61. For $C_{16}H_{22}O_2N_2·HAuCl_4$: Au, 32.72. Found: Au, 32.82.

## Summary

*Lupinus sericeus* Pursh. collected in Colorado contained when dried 3.68% of alkaloids consisting of spathulatine, previously described, and nonalupine, a new lupine alkaloid. A reinvestigation of the chemistry of spathulatine has confirmed the empirical formula previously assigned to this base. Nonalupine is not basic enough to form salts with strong acids.

WASHINGTON, D. C. RECEIVED JANUARY 4, 1940

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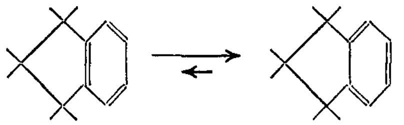
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

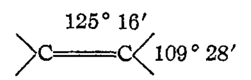
# Aromatic Stabilized Double Bonds. Mills–Nixon Problem

BY RICHARD T. ARNOLD AND ROBERT L. EVANS

The fundamental stereochemical problem proposed by Mills and Nixon[1] can be summarized by the equilibrium



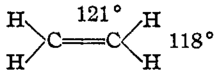
The assumptions in this interesting and clever proposal are: (a) that the structure of the olefinic double bond is represented by



and (b) that there exists a simple relation between bond types and bond angles.

Many experimental and theoretical approaches have been made toward a solution,[2,3,4] but the evidence submitted is most contradictory and leaves the problem completely unsolved. Objections have been raised to practically all of the experimental evidence thus far produced.[5]

The structure of ethylene recently has been determined, apparently with some degree of accuracy, and gives the following picture:[6,7]



Pauling and Brockway[8] have shown however that the angles in tetramethylethylene are nearly tetrahedral. These models, if true, question the validity of a simple correlation between bond angles and bond types. The foremost use of this assumption lies at the basis of the Sidgwick–Springall experiments. The structural work just completed on formaldehyde again raises a serious objection to this correlation.[9]

The wave mechanical treatment of the Mills–Nixon problem leads to the conclusion that substitution reactions (with high activation energies) cannot be used to locate stabilized aromatic double bonds. That this conclusion is in accordance with the experimental evidence is shown by the following

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(1) Mills and Nixon, *J. Chem. Soc.*, 2510 (1930).

(2) Sidgwick and Springall, *J. Chem. Soc.*, 1532 (1936).

(3) McLeish and Campbell, *ibid.*, 1103 (1937).

(4) Sutton and Pauling, *Trans. Faraday Soc.*, **31**, 939 (1935).

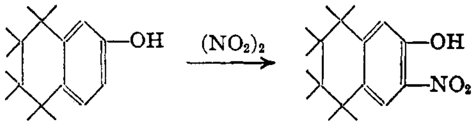
(5) Brockway and Taylor, *Brit. Ann. Reports*, **34**, 219 (1937).

(6) H. W. Thompson, *Trans. Faraday Soc.*, **35**, 697 (1939).

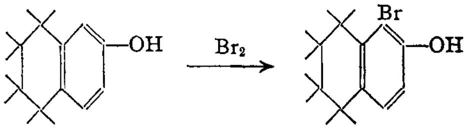
(7) Private communication from Professor Verner Schomaker of the California Institute of Technology.

(8) Pauling and Brockway, THIS JOURNAL, **59**, 1223 (1937).

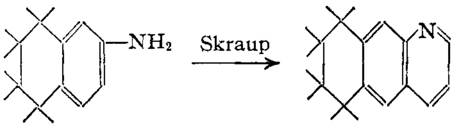
(9) Stevenson, LuValle and Schomaker, *ibid.*, **61**, 2508 (1939).



(10)

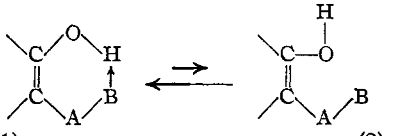


(1)



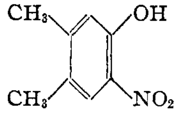
(11)

It is seen that the double bond can be placed in either of the two possible positions depending on the reaction chosen. During the past two years, an attempt has been made in this Laboratory to develop a physical method for locating double bonds which is free from objections. Using the naphthalene nucleus, the structure of which is well accepted, it has been shown[12] that if a hydroxyl and negative (electron attracting) group are placed around a stabilized double bond, an abnormally strong acid results. It has been proved[13] that chelate ring structures involving stabilized double bonds are unusually strong. In connection with correlations between the acidity of the hydroxy group and chelate rings involving stabilized double bonds, one must recognize two effects. This can be described by making use of a general equation

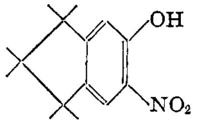


(1) (2)

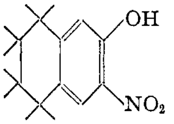
The inductive effect of (AB) is easily passed across the stabilized double bond. However, around this stabilized double bond the hydrogen bond is abnormally strong and, thermodynamically, results in a higher concentration of (1). Since it is easy for the proton to dissociate from (2) the overall effect of hydrogen bond formation is a slight diminution in the acidity. It must be recognized however that the inductive effect is usually the more important. This method has been extended, with a full realization of its limitations, to the Mills–Nixon problem by a careful study of the following molecules



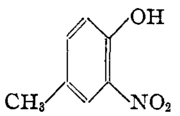
(A)



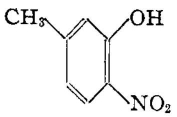
(B)



(C)



(D)



(E)

The acidity of the hydroxyl group here has been found to depend on four factors: namely, (a) the type of activating group present; (b) the strength of the chelate ring; (c) the inductive effect of all the dipoles present; and (d) the carbon–carbon bond type between the hydroxyl and activating group. As far as possible the first three factors have been held constant in A, B and C. Differences in dissociation constants for these substances must then indicate a dissimilarity in bond type. Actually the acidities of A, B and C are almost identical. A study of any interaction (*ortho*-effect) between the two methyl groups in A has been made by determinations on D and E. Such interactions seem to be active but appear to be constant in A, B and C. This has been recognized in dipole moment studies.

The possibility of stabilization in hetero rings containing one or more oxygen atoms, which according to our calculations is more probable than in hydrindene, is being investigated intently. Table I summarizes the data upon which the above mentioned statements are based.

TABLE I

Solvent: Ethanol–Water (50% by weight)

| Compound | T, °C. | pK |
|---|---|---|
| 2-Nitrophenol | 29 | 8.20 |
| 4,5-Dimethyl-2-nitrophenol | 28 | 8.81 |
| 4,5-Dimethyl-2-nitrophenol | 37 | 8.90 |
| 5-Hydroxy-6-nitrohydrindene | 37 | 8.96 |
| 6-Hydroxy-7-nitrotetralin | 37 | 9.05 |
| 4-Methyl-2-nitrophenol | 28 | 8.57 |
| 5-Methyl-2-nitrophenol | 28 | 8.43 |

## Experimental

**5-Hydroxyhydrindene.**—Thirty-five grams of 5-acetamidohydrindene was hydrolyzed with concentrated hydrochloric acid in several treatments to give 31 g. of the amine. To this sample in 45 cc. of concentrated hydrochloric acid and 70 cc. of water was added 21 g. of sodium nitrite in a saturated solution. To the clear solution was added 50 cc. of borofluoric acid (40%), and the white crystals which formed were filtered immediately. Decomposition of the crystals and filtrate (separately) using 44 cc. of sulfuric acid in 177 cc. of water gave after

(10) Thoms and Kross, *Archiv. Pharm.*, **265**, 336–347 (1927).

(11) Von Braun and Gruber, *Ber.*, **55**, 1710 (1922).

(12) Arnold and Sprung, THIS JOURNAL, **60**, 1163 (1938).

(13) Arnold and Sprung, *ibid.*, **61**, 2475 (1939).

steam distillation 12.5 g. of the phenol; b. p. 148–152° (30 mm.).[14,15]

**5-Hydroxy-6-nitrohydrindene.**—(a) The above 5-aminohydrindene was diazotized and nitrated in one step according to Neunhoffer[16] but on steam distillation an impurity accompanied the product. This unknown material melted at 82–83°.

(b) Following Diepolder's general method,[17] 5-hydroxyhydrindene was nitrated directly. The impurity (m. p. 82–83°) was again obtained but it was found that the high solubility of the desired compound in petroleum ether (b. p. 60–68°) allowed it to be decanted away from the more insoluble impurity and then crystallized; m. p. 63.5–64.5°.

**6-Hydroxy-7-nitrotetralin.**—Raney nickel catalytic hydrogenation of β-naphthol gave 50–60% yields of 6-hydroxytetralin at 190° and 500 lb. pressure (33.3 atm.). This phenol was nitrated with nitrogen dioxide and after steam distillation gave a 21% yield of the product which was recrystallized from ethanol; m. p. 88.5–89°. The acetate prepared from acetyl chloride in pyridine melted at 100°.[10]

**6-Methoxy-7-nitrotetralin.**—Using two equivalents each of 2.0 *N* sodium hydroxide and methyl sulfate, we obtained from 3.05 g. of the phenol, 1.37 g. of the ether. The substance was pale yellow and melted at 50–51.5°.

*Anal.* Calcd. for $C_{11}H_{13}O_3N$: C, 63.73; H, 6.32. Found: C, 63.74; H, 6.54.

**4,5-Dimethyl-2-nitrophenol.**—This compound was prepared by the direct nitration of the phenol using Diepolder's method; m. p. 85–86°.[14]

**5-Methyl-2-nitrophenol.**—Technical *m*-cresol was nitrated in cooled glacial acetic acid with a small excess of nitric acid dissolved in glacial acetic acid. After steam distillation and recrystallization, it melted at 54.5–55°.[18]

**4-Methyl-2-nitrophenol.**—This substance was prepared in the usual manner from *p*-cresol.

## Summary

1. In the light of recent structural studies on ethylene and tetramethylethylene, some of the original assumptions of the Mills–Nixon postulate are questionable.

2. A set of physical measurements on nitrophenols indicates no appreciable stabilization of double bonds caused by ring structures.

3. It has been pointed out that substitution reactions do not offer an acceptable method for locating double bonds.

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[14] W. Baker, *J. Chem. Soc.*, 476 (1937).

[15] Smith and Haller, This Journal, **61**, 143 (1939).

[16] Otto Neunhoffer, *Ber.*, **68**, 1774 (1935).

[17] Emil Diepolder, *Ibid.*, **42**, 2916 (1909).

[18] Staedel and Kolb, *Ann.*, **259**, 210 (1890).

MINNEAPOLIS, MINNESOTA RECEIVED OCTOBER 23, 1939

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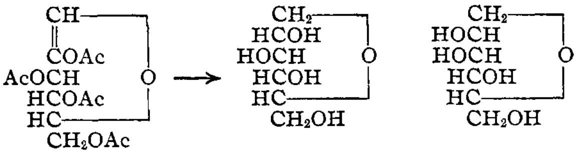
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

# The Chemistry of Naturally Occurring Monoanhydrohexitols. II. Synthetic Tetramethylstyracitol[1]

BY WERNER FREUDENBERG AND JOHN T. SHEEHAN

In 1930 Zervas[2] reported the synthesis of styracitol, the naturally occurring monoanhydrohexitol in *styrax obassia.* Tetraacetyl oxyglucal (I) was hydrogenated and subsequently deacetylated to 1,5-anhydro-*d*-sorbitol (II) or 1,5-anhydro-*d*-mannitol (III) depending on whether a *cis* or a *trans* addition occurred at the double bond.



(I) (II) (III)

The synthetic material was identical with the natural product. The question, however, if styracitol should be classified as a sorbitol or a mannitol derivative was not answered.

In a recent publication from this Laboratory we[3] attempted to ascertain the configuration of styracitol by a comparison of the rates of oxidation with lead tetraacetate and by an application of the isorotation rules to styracitol and its isomer polygalitol. These two substances were assumed to be epimeric since they formed on oxidation the same anhydrofructosazone[4] and glucosazone.[5] On the basis of this assumption the experimental results favored the mannitol structure for styracitol and the sorbitol structure for polygalitol.

To establish definitely the configuration of styracitol as a sorbitol or mannitol derivative, it was deemed necessary to devise a synthesis of a derivative of styracitol starting with glucose or mannose wherein all asymmetric centers are protected and remain unaltered throughout the series

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[1] Reported before the Organic Division, A. C. S. Meeting, Boston, Mass., September, 1939.

[2] Zervas, *Ber.*, **63**, 1689 (1930).

[3] Freudenberg and Rogers, This Journal, **59**, 1602 (1937).

[4] Bergmann and Zervas, *Ber.*, **64**, 2032 (1931).

[5] Shinoda, Sato and Sato, *Ibid.*, **65**, 1219 (1932).