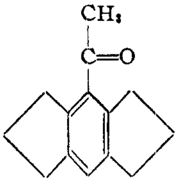
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Steric Effect of Methylene Groups. II

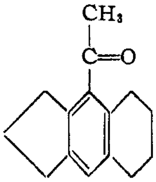
BY RICHARD T. ARNOLD AND ESTELLE RONDESTVEDT

In an earlier publication[1] it was pointed out that a Mills–Nixon[2] distortion of the ortho valence angles in hydrindene should lead to a diminution of the steric influence of the methylene groups adjacent to the benzenoid ring in cyclopentenobenzenes (*i.e.*, hydrindene types).

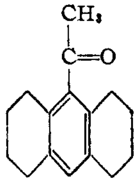
Experimental support for this view was found[3] in the observation that 4-acetylhydrindacene (I) undergoes the normal haloform reaction in contrast to 9-acetyloctahydroanthracene (III) which acts like a highly hindered ketone and forms a relatively stable trichloro ketone when treated with alkaline hypochlorite.



(I)



(II)



III

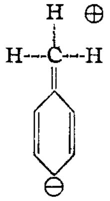
When treated with methylmagnesium iodide in a semi-micro Grignard apparatus (Zerewitinoff determination), compounds I, II and III undergo enolization to the extent of 30, 62 and 95%, respectively.

It is now recognized that the Raman frequency associated with the carbonyl group in alkyl aryl ketones has two characteristic values.[4] If there are no large ortho substituents flanking the carbonyl group, the plane in which this group resides is parallel to the benzenoid ring due to the fact that this structure is resonance stabilized. In such cases the characteristic carbonyl frequency (Raman) is approximately 1690 cm.$^{-1}$. Large ortho substituents force the carbonyl group out of the plane of the benzenoid ring and the resulting hindered carbonyl group has a Raman frequency of about 1705 cm.$^{-1}$.

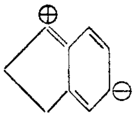
The measured Raman line (1690 cm.$^{-1}$) of acetophenone is found at 1687 cm.$^{-1}$ in compounds I and II. By contrast, the carbonyl frequency for III was found to be 1708 cm.$^{-1}$ and is thus practically our measured value (1707 cm.$^{-1}$) for acetomesitylene (2,4,6-trimethylacetophenone).[5]

Although the two pieces of evidence reported above are of quite different character it is apparent that each supports our early contention that the steric influence of an ortho methylene group in a six-membered ring is greater than that for the corresponding group in a five-membered ring.

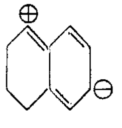
Methylenic reactivity in alkylbenzenes[6] appears to be due in part to the positive charge associated with the carbon atom attached directly to the benzene ring.



IV



V

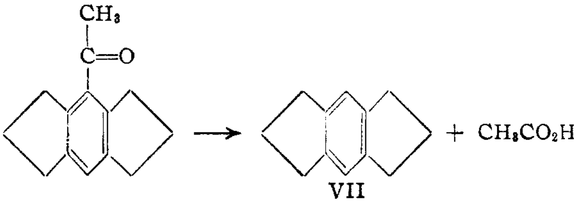


VI

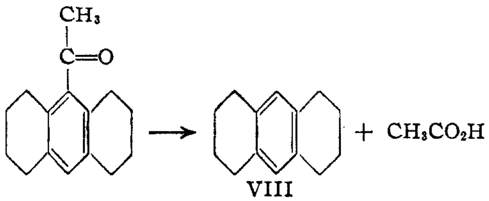
The magnitude of the positive charge depends upon hyperconjugation and is attributable to limiting structures of the type IV, V and VI for toluene, hydrindene, and tetralin, respectively.

An examination of molecular models indicates that (V) is more highly strained than (VI) if the ortho valence bonds in hydrindene are distorted toward one another as claimed above. Structure (V) should thus contribute to a lesser extent to the molecule hydrindene than does (VI) to the over-all structure of tetralin. As a result, the positive charge associated with the methylenic carbon atom in tetralin should be greater than that in hydrindene, and tetralin should have the more reactive methylene group. Quantitative experiments designed to test this hypothesis are now underway in this Laboratory. In this connection, it seems significant that tetralin forms a peroxide more rapidly than does hydrindene.[7]

When compounds I and III are heated under reflux with phosphoric acid (85%),[8] the acetyl groups are replaced by hydrogen to give hydrindacene (VII) and octahydroanthracene (VIII).



VII



VIII

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[1] Arnold and Barnes, THIS JOURNAL, **66**, 960 (1944).

[2] Mills and Nixon, *J. Chem. Soc.*, 2530 (1930).

[3] Arnold and Rondestvedt, THIS JOURNAL, **67**, 1265 (1945).

[4] Saunders, Murray and Cleveland, *ibid.*, **63**, 3121 (1941).

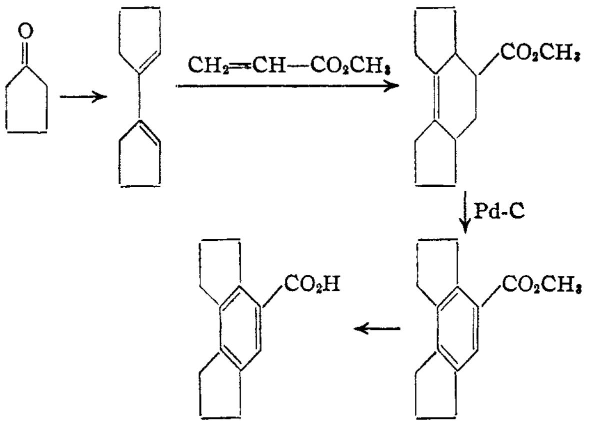
[5] These Raman data were kindly furnished by Drs. Bryce L. Crawford and Irving Rusoff of this Laboratory who will discuss the complete Raman spectra of these compounds in a separate publication. Maximum absolute error ±6 cm.$^{-1}$; relative error ±2 cm.$^{-1}$.

[6] Mulliken, Rieke and Brown, THIS JOURNAL, **63**, 41 (1941).

[7] Hock and Lang, *Ber.*, **75**, 1051 (1942).

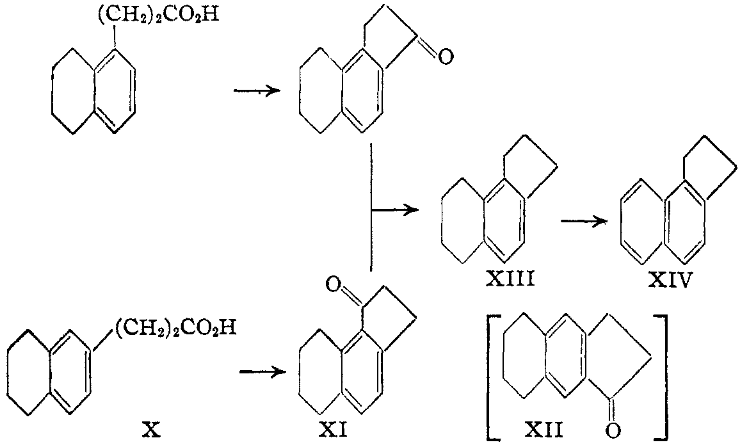
[8] Klages and Lickroth, *ibid.*, **32**, 1549 (1899).

In order to establish the formula for compound I more completely an acid (IX) isomeric with that derived from I was synthesized in the following manner.



IX

During the course of this study a convenient synthesis for 6,7,8,9-tetrahydrobenz(e)indane (XIII) was developed. This compound when dehydrogenated catalytically gave 1,2-cyclopentenonaphthalene (XIV) in good yield. The new synthesis is based upon the observation that β-6-tetralylpropionic acid (X) cyclizes to give (XI) rather than (XII) and thus permits use of the readily available mixture of β-5- and β-6-tetralylpropionic acids[9] as starting material.



XIII XIV

X XI XII

Acknowledgment.—The authors are grateful to the Graduate School of the University of Minnesota for financial aid made possible by the Fluid Research Fund.

Experimental

Zerewitinoff Determinations.—A semimicro apparatus making use of 80–100 mg. samples and designed by Drs. Lauer and Zaugg[10] of this Laboratory was employed.

6,7,8,9-Tetrahydrobenz(e)indanone-1 (XI).—Pure β-6-tetralylpropionyl chloride (45.5 g.) was dissolved in nitrobenzene (100 cc.) and treated dropwise with stannic chloride (115 g.) at 0–5°. The mixture, after standing overnight, was decomposed with ice and hydrochloric acid. Steam distillation of the nitrobenzene left a residue which was extracted with ether, dried and distilled under vacuum in a sausage flask. The solid product (23.7) melted at 39–41°. One recrystallization from petroleum ether (30–60°) gave a pure substance: m. p. 46–46.5°.

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.9: H, 7.53. Found: C, 83.5; H, 7.72.

6,7-Benzindanone-1.—One gram of the above product was intimately mixed with two equivalents of sulfur and the whole heated at 250° for two hours. Distillation under vacuum in a sausage flask followed by recrystallization from petroleum ether gave a pure ketone weighing 0.45 g.; m. p. 103°. This sample was identical with that prepared by the method of Mayer and Muller.[11]

6,7,8,9-Tetrahydrobenz(e)indane (XIII).—A mixture of β-5 and β-6-tetralylpropionic acids (prepared according to Arnold and Barnes[9]) was converted to a mixture of acid chlorides (b. p. 160–165° (10 mm.)) by treatment with thionyl chloride. This product (108 g.) was dissolved in nitrobenzene (200 cc.) and treated dropwise with stannic chloride (170 g.) at 0–5° over a period of forty-five minutes. Stirring was continued for three hours and the solution allowed to stand for an additional fifteen hours at room temperature. There was ultimately obtained by the usual method 62 g. of mixed ketones. Forty-two grams of this product when reduced by the Clemmensen method gave pure 6,7,8,9-tetrahydrobenz(e)indane (28 g.).

1,2-Cyclopentenonaphthalene (XIV).—The above hydrocarbon (33 g.) was dehydrogenated with palladium–charcoal (1.0 g., 10%) in the presence of carbon dioxide. After a reaction time of four hours there was obtained 27 g. of 1,2-cyclopentenonaphthalene; picrate m. p. 104–105°.[1]

Cleavage of 9-Acetyloctahydroanthracene.—One gram of ketone was heated under reflux for six hours with sirupy phosphoric acid (15 g.). After being cooled the mixture was diluted with water and extracted with benzene. Removal of the solvent gave platelets of octahydroanthracene (0.7 g., 88%); m. p. and mixed m. p. 68–70°.

Cleavage of 4-Acetylhydrindacene.—This reaction was carried out as described above. From the ketone (0.6 g.) there was obtained hydrindacene (0.2 g., 42%); m. p. and mixed m. p. 53–54°.

4-Aceto-5,6,7,8-tetrahydrobenz(f)indane (II).—To a solution of aluminum chloride (37.4 g.) in tetrachloroethane (390 cc.) maintained at 0–3° there was added over a period of fifteen minutes and with vigorous stirring 5,6,7,8-tetrahydrobenz(f)indane (28 g.) dissolved in tetrachloroethane (50 cc.). A solution containing acetic anhydride (18 g.) and tetrachloroethane (50 cc.) was added dropwise during the course of one hour. After an additional three hours at 0°, the mixture was poured onto ice and hydrochloric acid and worked up in the usual manner; yield 26.4 g.; b. p. 142–148° (1 mm.).

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.14. Found: C, 83.74; H, 7.83.

This ketone on treatment with potassium hypochlorite gave a chlorine containing product which was not identified further.

Methyl 1,2,5,6-Tetrahydro-2,3,4,5-dicyclopentenobenzoate.—1,1-Dicyclopentenyl[12] (27.5 g.) was treated with methyl acrylate (20 g.) at 190–200° for twelve hours. Direct fractionation gave 18.5 g. of product; b. p. 115–120° (1–2 mm.).

Anal. Calcd. for $C_{14}H_{20}O_2$; C, 76.3; H, 9.1. Found: C, 76.01; H, 9.3.

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[9] Arnold and Barnes, THIS JOURNAL, 65, 2393 (1943).

[10] Lauer and Zaugg, in press.

[11] Mayer and Muller, *Ber.*, 60, 2278 (1927).

[12] Barnett and Lawrence, *J. Chem. Soc.*, 1104 (1935).

2,3,4,5-Dicyclopentenobenzoic Acid (IX).—The above tetrahydro ester (18 g.) was heated at 300–305° for three hours in the presence of palladinized charcoal (1.0 g., 10%). The product was dissolved in ether, filtered, and fractionated. There was obtained an ester (10 g.); b. p. 110–115° (2–3 mm.). Saponification of a portion of this ester gave the desired acid; m. p. 200–202°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.2; H, 6.9; neut. equiv., 202. Found: C, 77.14; H, 6.5; neut. equiv., 199.

Summary

1. Further evidence is presented to show that the steric effect of the methylene group in hydrindene is smaller than that in tetralin.

2. A new and convenient synthesis of 1,2-cyclopentenonaphthalene is described.

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[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY, DEPARTMENT OF FOOD SCIENCE AND TECHNOLOGY, NEW YORK STATE AGRICULTURAL EXPERIMENT STATION, CORNELL UNIVERSITY]

The "Browning (Maillard) Reaction" in Heated Solutions of Uronic Acids[1]

BY JOAN L. SEAVER AND Z. I. KERTESZ

The increased production of dehydrated food during World War II intensified the interest in the formation of colored compounds from carbohydrates and amino acids. These reactions, first studied by Maillard,[2] are now believed to play important roles in the detrimental color changes which occur in many food products during manufacture and storage. During recent years research on this topic was greatly expanded and a number of excellent reviews dealing with the various aspects of the problem have been prepared.[3] A perusal of the literature reveals a complete lack of information on the behavior of uronic acids under conditions which produce the "browning reactions" with other carbohydrates. We wish to report below some observations which indicate that uronic acids are even more active in forming dark colored compounds than are the common carbohydrates under similar conditions.

It it commonly known that uronic acids heated with strong acid will form furfural and dark colored "furanoid bodies."[4] It is less appreciated that galacturonic acid in solution[5] or even in the dry form and comparatively free from impurities may turn brown. This suggested that the instability of galacturonic acid may go hand in hand with a high degree of reactivity with amino acids to form the type of coloration described by Maillard.

Experimental Methods

Conditions of Heating.—The solutions (10 cc.) were 0.1 *M* with respect to all individual constituents when heated in loosely closed Pyrex test-tubes in a water-bath at 98°. All solutions were adjusted to *p*H 4.3 which was taken as representing an approximate average value of the *p*H of common fruits and fruit products. It is known, however, that the reaction proceeds faster at *p*H values approaching neutrality or below 1.5.

Determination of Color Formed.—Upon completion of heating, the solutions were prepared for a measurement of the developed color by Anson's[6] method. After cooling, 2.8 cc. of 20% metaphosphoric acid solution and 7 cc. of acetone were added and the mixture made up with water to 25 cc. and filtered. Since no precipitate was formed from these solutions upon further dilution with water, the filtrates were used directly for the determination of the color. In a few experiments the color developed even in a few hours was too dark for dependable measurement and in these cases diluted solutions were used. Tests indicated that Beer's law held in these diluted samples.

The per cent. light transmission was measured in a Lumetron Colorimeter using a 370 mμ filter. A standardization curve with potassium dichromate was prepared and the results read in "mg % potassium dichromate equivalent." The choice of the wave length of 370 mμ was made on the basis of the shapes of a series of transmission curves obtained for the visible spectrum for potassium dichromate solution, caramel solution and brown solutions formed by the heating with glycine of glucose, galacturonic acid or ascorbic acid. All these compounds showed the well-known typical transmission curves gradually rising from an optical density of about zero at 550 mμ to a maximum at 350 mμ, the end of the range measured.

Materials Used.—All carbohydrates used were commercial C. P. grade. The galactonic[7] and mucic acids were prepared by the customary methods of oxidation with bromine and nitric acid, respectively. "Pectinic Acid I" was a sample of "Pectinum N.F.VII" obtained from the California Fruit Growers' Exchange; "Pectinic Acid II" an older unstandardized preparation from the same source. The hydrogen peroxide-degraded pectinic acid was prepared by keeping a mixture of 10 cc. of 3% pectinic acid plus 1 cc. of 30% hydrogen peroxide at room temperature for three days. The typical high viscosity of the pectinic acid solution disappeared completely during this period. The solution was then evaporated to dryness in vacuum at room temperature and the residue redissolved in water.

The α-methyl-D-galacturonic acid methyl ester was prepared by the method of Morell and Link.[8]

Results and Discussion

Tables I and II show the formation of color during the heating of D-galacturonic acid solutions. The extent of color formation both with and without glycine exceeds the coloration which will occur

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[1] Journal Paper No. 681, New York State Agricultural Experiment Station, Geneva. Jean Griffin participated in the early phases of this work.

[2] Maillard, *Compt. rend.*, **54**, 66 (1912).

[3] Joslyn, *Ind. Eng. Chem.*, **33**, 308 (1941); etc.

[4] Lefévre, Dissertation, Göttingen, 1907.

[5] Link and Nedden, *J. Biol Chem.*, **94**, 307 (1931).

[6] Anson, Proc. Subs. Res. Development Lab. Conference, Chicago No. 1, p. 45, 1945.

[7] Weare indebted to R. J. McColloch of this Laboratory for the preparation of the galactonic acid. The free acid was prepared from the sodium salt by the use of IR-100 Amberlite ion exchange resin.

[8] Morell and Link, *J. Biol. Chem.*, **100**, 385 (1933).