TABLE II

ABSORPTION MAXIMA OF SOME 7-SUBSTITUTED-8-QUINOLINOLS IN THE VISIBLE

Cpd.	Solvent	Maxima (mμ)		Cpd.	Solvent	Maxima (mμ)
I	0.1 *N* HCl	500–510(4.21)[a]	530(4.24)	I	0.1 *N* NaOH	480(4.13)
II	0.1 *N* HCl	510(4.32)	540(4.32)	II	0.1 *N* NaOH	465(4.17)
III	0.1 *N* HCl	505(4.23)	535(4.25)	III	0.1 *N* NaOH	475(4.14)
IV	0.1 *N* HCl	510(4.29)	540(4.29)	IV	0.1 *N* NaOH	470–475(4.16)
V	0.1 *N* HCl	510(4.20)	530–540(4.20)	V	0.1 *N* NaOH	480(4.19)

[a] Figures in parentheses are logarithms of the molecular extinctions.

tests were obtained in the acid solution; in the buffer copper and iron reacted with all the compounds, magnesium with none.

The absorption spectra of all the compounds in acid and base solutions were determined in the visible region (Table II). Since the compounds are red in acid and yellow in base, it seemed possible that they could be used as acid–base indicators. Therefore, a study of the variations in spectra with changing *p*H was made with compounds II and IV. As shown by a graph of extinction against *p*H (Fig. 1) three different structures exist in acid, neutral and basic solution. It was not considered worthwhile to calculate an accurate indicator constant from these data, since the color transition is evidently more gradual than desirable for a practical indicator.

The compounds are capable of functioning as irreversible indicators for titrations with standard bromine solutions because they change from red to colorless with an excess of bromine. It is therefore possible to use these derivatives of 8-quinolinol as indicators for the well-known bromine titration of 8-quinolinol.

Experimental

Preparation of Compounds.—8-Quinolinol-5-sulfonic acid or 8-hydroxyquinaldine-5-sulfonic acid was coupled with diazotized anilines in alkaline solution according to the directions of Matsumura.[3] The sodium salts were converted to the free bases by addition of acetic acid and recrystallized from alcohol in which they are sparingly soluble. The purity of the compounds was tested by running a Beer law check in acid solution at 530 mμ on 5 or 6 known concentrations by weight and extrapolating the straight lines obtained to zero concentration. Since the corresponding extinctions did not differ from zero by a significant amount (less than 0.05 unit), the compounds were considered sufficiently pure.

Absorption Spectra.—The extinctions of solutions containing 0.0240 g./liter of each compound were determined at 5-mμ intervals from 400–700 mμ with a Beckman model DU spectrophotometer using 1.00-cm. cells. (The measurements in acid solutions on compound V required a 0.0160 g./l. concentration because of the insolubility of this compound.) The *p*H of the solutions was measured with a Beckman *p*H meter to the nearest 0.1 unit, adjustment of *p*H to the desired values being made by the use of standard phthalate, phosphate and boric acid buffers. A check on possible interference with the color from these buffer constituents was obtained by adjusting the *p*H of several of the solutions with standard acid and base only; no differences were noted. Variations in ionic strength of the many solutions used were not large enough to make significant differences in extinction.

Qualitative Tests.—Fifteen ml. of a solution containing 0.040 g./l. of each compound was treated with 1 ml. of an approximately 1% solution of the desired metal ion, buffered with potassium acid phthalate and acid to a *p*H of 3.5, and diluted to 25 ml. As blanks solutions containing 15 ml. of the reagent solution in the buffer, and 1 ml. of the metal ion in the buffer, were used. A positive test was claimed if the extinction of the test solution differed by more than 0.1 unit from the combined values for the blanks. The tests were run at 7 wave lengths between 400 and 550 mμ.

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CHEMISTRY DEPARTMENT
UNIVERSITY OF LOUISVILLE
LOUISVILLE, KENTUCKY

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[3] K. Matsumura, THIS JOURNAL, **49**, 810 (1927).

The Structure of Sedoheptulosan[1]

BY JAMES W. PRATT, NELSON K. RICHTMYER AND C. S. HUDSON

In 1938, one of us[2] marshalled the available evidence and presented what appeared to be an unequivocal proof that sedoheptulosan possessed the unusual structure I, with one of its rings having an ethylene oxide form and the other a septanoid form. The evidence behind this reasoning stemmed from three different sources: (1) Ettel's proof,[3] which has since been confirmed by other researches, that sedoheptulose is D-altroheptulose; (2) Hibbert and Anderson's preparation[4] of a crystalline tetramethylsedoheptulosan which upon oxidation with warm concentrated nitric acid yielded a trimethoxyglutaric acid; the latter was characterized as a dimethylamide melting at 145–146°, and was assumed to have the ribo configuration because it was optically inactive (the inactive xylo derivative could be excluded because of its higher melting point, 167–168°); and (3) Levene and Compton's oxidation[5] of 2,3,4-trimethyl-D-ribose similarly to a trimethoxyglutaric acid whose optically inactive dimethylamide also melted at 145–146°. From these results it was concluded that only formula I could apply to sedoheptulosan.

However, recent investigations in this laboratory have produced evidence that is not in accord with the formulation I. Oxidation of sedoheptulosan with periodate indicated the presence in its molecule of three contiguous secondary hydroxyl groups,[6] and restricts the possible formulas to I, II, and III. We have now found that the catalytic hydrogenation of the dialdehyde obtained from the periodate oxidation of sedoheptulosan, followed by acid hydrolysis of the product (IV, V, or VI), produced a non-reducing, water-soluble liquid which

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[1] A portion of this material has been taken from the thesis to be submitted by James W. Pratt to the Chemistry Department of the Graduate School of Georgetown University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

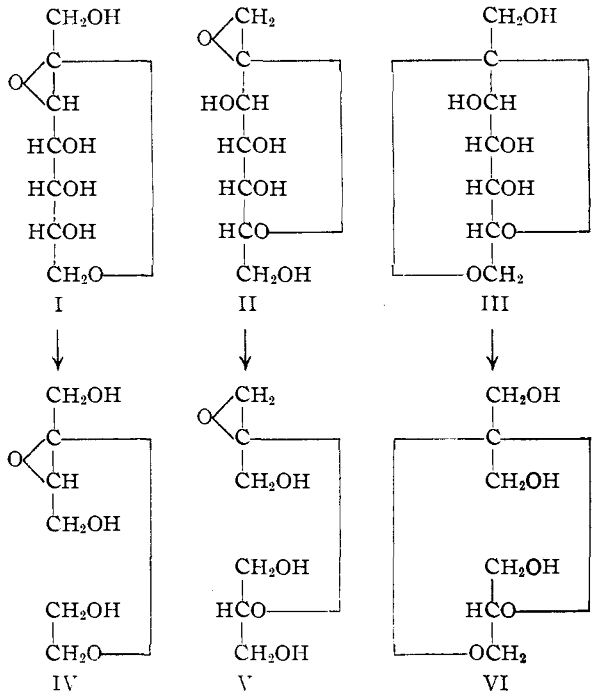
[2] C. S. Hudson, THIS JOURNAL, **60**, 1241 (1938).

[3] V. Ettel, *Collection Czechoslov. Chem. Communs.*, **4**, 513 (1932).

[4] H. Hibbert and C. G. Anderson, *Can. J. Research*, **3**, 306 (1930).

[5] P. A. Levene and J. Compton, *J. Biol. Chem.*, **116**, 169 (1936).

[6] W. T. Haskins, R. M. Hann and C. S. Hudson, unpublished results. *Cf.* N. K. Richtmyer, *Advances in Carbohydrate Chem.*, **1**, 52 (1945).



upon treatment with p-nitrobenzoyl chloride furnished a 30% yield (based on the weight of the reduced dialdehyde) of glycerol tri-(p-nitrobenzoate) of m.p. 193–195°. The fate of the remainder of the molecule has not been determined, but it does not seem possible that it could have been converted to glycerol under the experimental conditions.

Isolation of the p-nitrobenzoate of glycerol rather than that of ethylene glycol (m.p. 141°), which would be expected if sedoheptulosan had formula I, can be explained only on the basis of formula II or III. Of these we prefer formula III because of the failure of tetratosylsedoheptulosan to react with sodium iodide at 100° even though it must contain a primary tosyloxy group. This sluggish behavior has been reported as a characteristic of the primary tosyloxy group adjacent to the carbonyl group in 1-tosyl-2,3,4,5-diisopropylidene-D-fructose,[7] 1,4-ditosyl-2,3-isopropylidene-D-xylulose,[7] and 1-tosyl-2,3:4,6-diisopropylidene-L-sorbose.[8] On the other hand, a normal replacement of the primary tosyloxy group by an iodine atom should be expected from the tetratosyl derivative of II.

From these experiments, and certain other data that are in themselves inconclusive, it now appears that sedoheptulosan should be represented by formula III, and that it has the same ring structure that occurs in the known 1,6-anhydrides of glucose, mannose, altrose, galactose, and idose. A repetition of the methylation studies is now under way in an attempt to resolve the contradiction with the earlier work.

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AND METABOLIC DISEASES
NATIONAL INSTITUTES OF HEALTH
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BETHESDA, MARYLAND

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[7] P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, **120**, 607 (1937).

[8] T. S. Gardner and J. Lee, *J. Org. Chem.*, **12**, 733 (1947).

Aromatic Cyclodehydrogenation. X. Studies on Ring Oxygen Compounds. Dinaphtho[1,2,1',2']-furan[1]

BY MILTON ORCHIN AND LESLIE REGGEL

In connection with another problem,[2] it became of interest to synthesize 1-(o-tolyl)-1-(2'-naphthyl)-1,2-dihydronaphthalene (IV). A possible route to IV appeared to be the reaction of o-tolylmagnesium bromide with 1-keto-2-(1'-tetralylidene)-1,2,3,4-tetrahydronaphthalene (I); 1,2-addition to the carbonyl group would give the carbinol, II, whereas 1,4-addition to the conjugated system would give the desired intermediate ketone, III. It was thought that if 1,4-addition took place, III might be separated *via* the semicarbazone and then be reduced and dehydrogenated to yield IV. The anticipated results were not obtained, however. About 61% of the starting ketone, I, was recovered when the Grignard reaction mixture was decomposed and the solvents removed. The balance of the product was treated with semicarbazide, and the ketonic material was recovered by hydrolysis and reduced by the Huang-Minlon modification of the Wolff–Kishner method; the crude reduced material was dehydrogenated, but no pure product could be isolated. The material that did not form a semicarbazone, presumed to be the carbinol, II, formed by 1,2-addition, or its dehydration product, was catalytically dehydrogenated. A small amount of 1-(o-tolyl)-2-(1'-naphthyl)-naphthalene (V) was isolated, but the main product was a colorless substance, $C_{20}H_{12}O$, melting point 155.0–156.5°, which formed a red 2,4,7-trinitrofluorenone complex, an orange s-trinitrobenzene complex, and an orange dipicrate, m.p. 164.5–165.2°. Interestingly enough, the ultraviolet absorption spectrum of this compound proved to be identical with that of a compound we had previously shown to be present in a mixture obtained by direct cyclodehydrogenation of the ketone, I.

In the earlier work it was shown that treatment of the ketone, I, with a palladium-on-charcoal catalyst resulted[3] in the formation of a mixture from which it was possible to isolate dibenzo[c,kl]-xanthene (VIII); ultraviolet absorption spectra showed the presence of another substance, which could not be obtained pure, to which the structure of dinaphtho[1,2,1',2']furan (VII) was assigned. The spectrum of VII, as previously obtained from mixtures of VII and VIII, was identical with the spectrum of the compound of melting point 155.0–156.5° obtained in the present work; no trace of VIII could be detected. The isolation of the dinaphthofuran, VII, in the present investigation, strengthens the case for the assigned structure but it cannot as yet be considered as completely substantiated.

In attempting to account for the formation of the furan, VII, it was thought that the Grignard reagent might have reduced I to VI, and that VI, present in the fraction that did not form a semicarbazone, might have produced VII on dehydro-

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[1] Not subject to copyright.

[2] M. Orchin, L. Reggel and R. A. Friedel, THIS JOURNAL, **73**, 1449 (1951).

[3] M. Orchin, L. Reggel and R. A. Friedel, *ibid.*, **71**, 2743 (1949).