TABLE I

OXIDATION OF POLYHYDRIC ALCOHOLS WITH SODIUM PERBORATE

Alcohol	Wt. of alcohol in g.	Wt. of ferrous sulfate in g.	Acetic acid Volume in cc.	Acetic acid Strength in N	Wt. of sodium perborate in g.	Time of reaction in min.	Yield of oszaone, g.	Yield of oszaone, %	Melting point of osazone in °C. Found (uncorrected)	Melting point of osazone in °C. Fenton and Jackson[2]
Ethylene glycol	1.55	1.3	30	4	4.293	60	0.588	9.88	168	169.5
Glycerol	2.5	0.25	35	8	4.668	15	0.96	13.25	131	130–131
Erythritol	2.5	1.25	25	8	3.508	30	1.53	25.0	166	167
Mannitol	5.0	1.25	35	3	4.720	360	1.55	20.9	198	197–198
Dulcitol	2.0	1.0	15	3	1.89	480	...	...	205	206
Sorbitol	2.0	0.9	15	3	1.89	480	...	...	204	203

TABLE II

YIELDS OF OSAZONES

Alcohol	Hydrogen peroxide, Fenton and Jackson g.	Hydrogen peroxide, Present investigation g.	Hydrogen peroxide and boric acid (1 mol), g.	Sodium perborate alone, g.	Boric acid 1 mol. g.	Boric acid 2 mols. g.	Boric acid 3 mols. g.
Ethylene glycol	0.70	0.55	0.50	0.588	0.55	0.54	0.54
Glycerol	1.55	1.00	0.85	0.960	0.81	0.78	0.76
Erythritol	1.75	1.55	1.30	1.530	..	..	..
Mannitol	3.12	2.15	1.84	1.550	1.27	1.08	0.20

oxidation product with sodium perborate is a little less than with hydrogen peroxide except with ethylene glycol but there is a distinct advantage in the use of sodium perborate which can be added conveniently in any controlled quantities to a reaction mixture. This investigation has also shown that the presence of boric acid has a retarding effect on the oxidation of a polyhydric alcohol both with sodium perborate as well as with hydrogen peroxide.

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A Correction: Absorption Spectra of Azlactones[1]

BY F. W. SCHUELER AND CALVIN HANNA

RECEIVED JULY 7, 1952

Recently we have had our attention called to errors in some of the absorption maxima values we reported for certain azlactones.[2]

The corrected values for the azlactones reported in the above reference are listed in Table I. As will be seen upon comparison of these values with the values reported in the above-mentioned reference, the average errors for the first maxima and second maxima were 35 and 74 mμ, respectively. Such errors are clearly of such a constancy that they suggested a systematic error in the standardization of the instrument during the period through which these materials were studied.

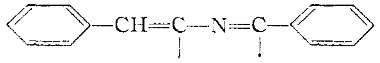
It has been the practice in many laboratories to check the standardization of the Beckman spectrophotometer only twice or three times a year. Following our experience with this instrument, however, we feel that the instrument should be checked before each use with a compound of known spectra before the determination of the spectra of compounds never before evaluated in these regards.

TABLE I

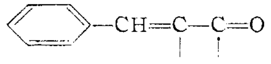
ABSORPTION SPECTRA OF AZLACTONES

No.	Max. 1 mμ	Max. 2 mμ	No.	Max. 1 mμ	Max. 2 mμ
1	259	377	15	265	386
2	268	387	16	244	365
3	271	376	17	257	370
4	261	365	18	232	328
5	259	360	19	264	369
6	259	376	20	265	401
7	264	393	21	264	396
8	257	373	22	264	394
9	260	362	23	259	383
10	...	359	24	260	361
11	...	360	25	225	286
12	...	290	26	245	482
13	259	372	27	240	475
14	247	366	28	240	425

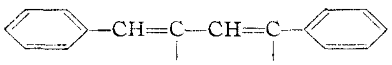
As a result of this correction it will be seen that the conjugated system

2 

better accounts for the spectra of the azlactones than the system

1 

originally indicated.[2] Moreover, a comparison of these corrected results on the azlactones, together with results obtained using the analogous crotonolactones,[3] indicates that chromophoric system operates in both. Thus, in the case of the crotonolactones, the conjugated system



is analogous to the system (2) indicated above for the azlactones.

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[1] This work was aided by a grant from the U. S. Public Health Service.

[2] F. W. Schueler and S. C. Wang, THIS JOURNAL, **72**, 2220 (1950).

[3] F. W. Schueler and Calvin Hanna, *ibid.*, **73**, 3528 (1951).

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Indophenols of 8-Quinolinols

BY J. P. PHILLIPS, J. F. EMERY AND QUINTUS FERNANDO

RECEIVED JUNE 30, 1952

The indophenol formed by 8-quinolinol when treated with hydroxylamine in an alkaline oxidizing solution[1] should possess oxidizing and indicator properties like other indophenols,[2,3] and, since it still has the chelating group of 8-quinolinol, should show the reactions with metal ions characteristic of that compound. The only previous investigation is that by Berg,[4] who named the indophenol "indoöxine" and proposed its use as a precipitating agent for trace quantities of several metal ions. A further study by instrumental methods of the properties of indoöxine and some new derivatives seemed desirable.

Although indophenols from 2-methyl- and 3-methyl-8-quinolinol were readily prepared by Berg's method,[1] no reaction was obtained from 4-methyl-8-quinolinol. This failure to react may have been a steric effect since some impediment to substitution at the 5-position by the 4-methyl group would be expected.

Both acidic and basic solutions of indoöxine were found to be unstable. In 0.1 *N* sodium hydroxide a fresh solution has an absorption maximum in the visible at 705 mμ; after several days a sodium salt precipitates leaving a virtually colorless solution. In 0.1 *N* hydrochloric acid decomposition is more rapid: the initially red solution having an absorption maximum in the visible at 500 mμ fades to a light yellow (with maxima at 262, 338 and 394 mμ), decomposition being complete in 3–6 days. By comparison with the reaction of other indophenols with acids this change probably represents hydrolysis to 5-amino-8-quinolinol and 5,8-quinolinequinone.[5]

An investigation of the rate of the decomposition in acid solution by measuring the decrease in extinction at 500 mμ showed that the rate increased with increasing acidity (Table I). This behavior is similar to that of phenolindophenol,[6] although the rate did not appear to be first order as it is for phenolindophenol.

TABLE I

DECOMPOSITION RATE OF INDOÖXINE (5.6 MG./L.) IN HYDROCHLORIC ACID

Time, min.	Extinction at 500 mμ In 0.02 *N* acid	In 0.007 *N* acid
30	0.192	0.208
45	.180	.204
60	.162	.197
75	.146	.190
105	.120	.177
180	...	.082

Since ethanol solutions seemed to be stable, absorption spectra for characterization purposes were run in this solvent (Table II) even though Beer's law was not obeyed. In other solvents (Table II) considerable variations in color were noted. (Ultraviolet measurements were made only on the ethanol solutions.)

TABLE II

ABSORPTION MAXIMA IN THE SPECTRA OF 8-QUINOLINOL-INDOPHENOLS

Compound	In ethanol		Chloroform	Acetone
Indoöxine	246	545 mμ	530	515
2-Methylindoöxine	250	545	535	517
3-Methylindoöxine	254	552	533	520

A study of the variations in extinction at several wave lengths of indoöxine solutions as a function of *p*H (Fig. 1) showed that four different structures were present as indicated in the equation

$$\text{Red} \xrightarrow{p\text{H } 3.5} \text{Violet} \xrightarrow{p\text{H } 7} \text{Green} \xrightarrow{p\text{H } 12} \text{Blue}$$

It seems reasonable to regard these colors as corresponding to a dihydrochloride, hydrochloride, free base and sodium salt, respectively. Although indoöxine has been mentioned[4] as an acid–base indicator the complexity of the color changes does not recommend it for such use.

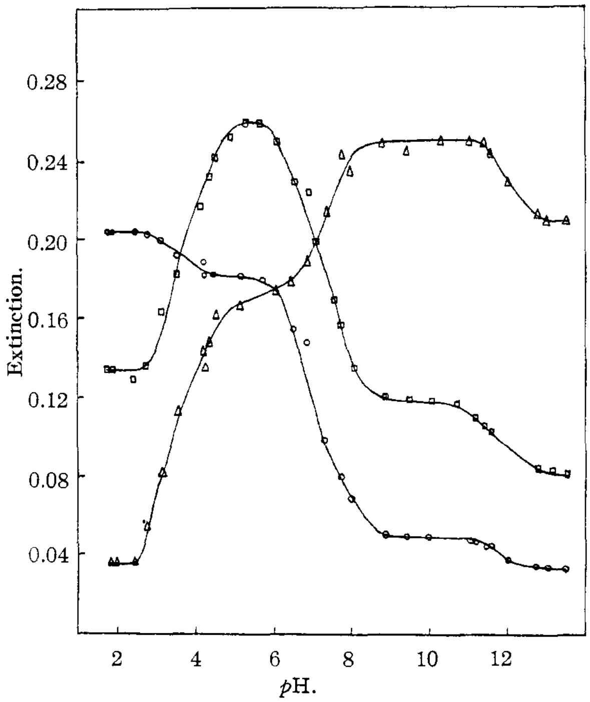

Fig. 1.—Variation of extinction of indoöxine with *p*H: ⊙, 500 mμ; ⊡, 550, mμ; △, 600 mμ.

The polarographic reduction of indoöxine in acid solutions was masked by catalytic waves as is usual with quinoline compounds and could not be interpreted. In basic solutions (*p*H 10–12) peculiar effects were obtained: polarograms on fresh solutions showed several small poorly defined waves; if the polarograms were run again immediately on the same solutions, only two waves, having half-wave potentials at −0.2 and −1.2 v. (*vs.* S.C.E.), were obtained. Additional runs on the same solution gave the same two waves but with increasing diffusion currents. Results of this sort may have been caused by reaction of the compound with the mercury in the cell, but at any rate did not seem promising for the development of analytical methods with indoöxine using polarography.

Qualitative tests were run with 2-methylindoöxine and several metal ions with results generally

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(1) R. Berg and E. Becker, *Ber.*, **73B**, 172 (1940).

(2) H. D. Gibbs, *Chem. Revs.*, **3**, 291 (1926).

(3) I. Stone, *Anal. Chem.*, **12**, 415 (1940).

(4) R. Berg and E. Becker, *Z. anal. Chem.*, **119**, 81 (1940).

(5) G. Heller, *Ann.*, **418**, 259 (1919).

(6) G. Schwarzenbach, H. Mohler and J. Sorge, *Helv. Chim. Acta*, **21**, 1636 (1938)

similar to those with indoöxine,[4] with the expected exception that aluminum was not precipitated.

Experimental

Preparation of Compounds.—5,8-Quinolinequinone-5-(8-hydroxy-5-quinolylimide) was prepared from 5.0 g. of 8-quinolinol, 2.5 g. of hydroxylamine hydrochloride and 150 ml. of 2 *M* sodium carbonate in 150 ml. of methanol by passing air through the solution for six hours. The precipitated sodium salt was filtered, converted to the free base by suspension in acetic acid and finally recrystallized from ethanol, yield 2 g. (38%). Calcd. for $C_{18}H_{11}N_3O_2$: N, 13.95. Found: N, 14.08.

5,8-Quinaldinequinone-5-(8-hydroxyquinaldylimide) was obtained in 29% yield from 8-hydroxyquinaldine by the above procedure, m.p. 222°. Calcd. for $C_{20}H_{15}N_3O_2$: N, 12.77. Found: N, 12.73.

The corresponding indophenol from 3-methyl-8-quinolinol was obtained similarly in 39% yield, m.p. 235°. Calcd. for $C_{20}H_{15}N_3O_2$: N, 12.77. Found: N, 12.84.

Indophenols were also obtained from 2-phenyl-8-quinolinol and 2-styryl-8-quinolinol but were not purified because of their extreme insolubility in the common solvents. No reaction was obtained from 4-methyl-8-quinolinol or 8-quinolinol-5-sulfonic acid.

Spectrophotometric Measurements.—All spectra were determined with a Beckman DU spectrophotometer using 1.00-cm. cells at room temperature (25 ± 3°). Absorption spectra in 95% ethanol, chloroform and acetone were run on concentrations of 3–5 mg./l. The decomposition rate in hydrochloric acid was studied both in 50% acetone and 50% ethanol solutions with similar results in both solvents. The variation of extinction with *p*H was performed at 500, 550 and 600 mμ with 40% ethanol solution having an indooxine concentration of 0.00944 g./l. Hydrochloric acid and sodium hydroxide were used to adjust the *p*H which was measured with a Beckman H-2 Meter.

Polarograms.—A Sargent Model XXI Polarograph with a dropping mercury cathode having characteristics previously described[7] was used. The concentration of indooxine was 4.0 mg./l. in Britton and Robinson buffers in which ethanol had to be added to keep the substance in solution.

Qualitative Tests.—Spot tests were performed using a saturated alcoholic solution of 2-methylindoöxine and approximately 1% solutions of metal ions. In an acetate buffer of *p*H 5, blue precipitates were obtained from Ag^+, Sn^{+++} and Hg^{++}. At *p*H 12 precipitates were obtained in addition from Cd^{++}, Co^{++}, Cu^{++}, Fe^{++}, Mg^{++}, Mn^{++}, Ni^{++}, UO_2^{++}, Fe^{+++}, La^{+++} and Th^{++++}. No precipitates were observed with Al^{+++}, Cr^{+++}, Na^+ and K^+.

Acknowledgment.—This work was supported in part by a grant from the Research Corporation.

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[7] Q. Fernando and J. P. Phillips, THIS JOURNAL, **74**, 3103 (1952).

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Isomerization of Saturated Hydrocarbons. X.[1] Catalytic Isomerization of Cycloheptane

BY HERMAN PINES, F. J. PAVLIK[2] AND V. N. IPATIEFF

RECEIVED JUNE 11, 1952

It has previously been shown that under certain controlled conditions aluminum bromide–hydrogen bromide does not cause isomerization of *n*-butane to isobutane[3] or alkylcyclopentanes[1,4] to cyclohexane and alkylcyclohexanes unless traces of olefins or alkyl halides were present. It was also shown that ultraviolet light[1,5] promotes the isomerization of these compounds in the presence of aluminum bromide–hydrogen bromide and that aluminum bromide in the presence of oxygen[1,6] and in the absence of hydrogen bromide causes a similar rearrangement. It was further shown that benzene inhibits isomerization.[1,7]

In order to explain the function of the various promoters an ionic mechanism was proposed[4,8] in which it was postulated that the alkyl halides added as such or formed *in situ*, acted as chain initiators.

These studies have now been extended to include cycloheptane and Table I summarizes the results obtained with this compound.

TABLE I

ISOMERIZATION OF CYCLOHEPTANE

From 3.5 to 4.8 grams of cycloheptane was used in each experiment. The reactions were made at 25°.

	Reagents used:	Moles per 100 moles of cycloheptane					
Expt.	$AlBr_3$	HBr	*s*-C_4H_9Br	Benzene	Oxygen	Time, hours	Methylcyclohexane, %
1	2	1				9	0
2	3.0	1				9	0
3	1.5	1	0.1			2	100
4	1.5	1	0.1	0.15		2	7
5	1.5				0.5	9	58
6	2	1				2[a]	2
7	2	1				9[a]	34

[a] Ultraviolet irradiation.

It was found that as in the case of butanes and alkylcyclopentanes, the isomerization of cycloheptane does not take place in the presence of a catalyst consisting of only aluminum bromide–hydrogen bromide (experiments 1 and 2).

If to these reactants is added 0.1 mole per cent. of *s*-butyl bromide, complete isomerization to methylcyclohexane occurs after two hours of contact (expt. 3) as compared to nine hours in the preceding two experiments. The addition of 0.15 mole per cent. of benzene greatly inhibits the isomerization reaction; only 7% of methylcyclohexane is formed (expt. 4).

The similarity of the isomerization of cycloheptane and alkylcyclopentanes was also shown by experiment 5 in which 0.5 mole per cent. of oxygen was introduced as a promoter and aluminum bromide in the absence of added hydrogen bromide was used as a catalyst; after a nine-hour contact time, 58% of methylcyclohexane was produced.

It was found that the isomerization of cycloheptane in the presence of an aluminum bromide–hydrogen bromide catalyst can also proceed in the absence of promoters, if the reactants are placed in a quartz tube and irradiated with ultraviolet light. After two hours of exposure about 2% and after nine hours 34% of cycloheptane undergoes isomerization. The mechanism of isomerization of cycloheptane is similar to that of alkylcyclopentanes and can be expressed as

$$RBr + AlBr_3 \rightleftarrows [R^+][AlBr_4^-]$$

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[1] For paper IX of this series see H. Pines, F. J. Pavlik and V. N. Ipatieff, THIS JOURNAL, **73**, 5738 (1951).

[2] Universal Oil Products Company Predoctorate Fellow 1949–1951.

[3] H. Pines and R. C. Wackher, THIS JOURNAL, **68**, 595, 2518 (1946).

[4] H. Pines, B. M. Abraham and V. N. Ipatieff, *ibid.*, **70**, 1742 (1948).

[5] H. Pines, E. Aristoff and V. N. Ipatieff, *ibid.*, **72**, 4055 (1950).

[6] H. Pines, E. Aristoff and V. N. Ipatieff, *ibid.*, **71**, 749 (1949).

[7] H. Pines, E. Aristoff and V. N. Ipatieff, *ibid.*, **72**, 4304 (1950).

[8] H. S. Bloch, H. Pines and L. Schmerling, *ibid.*, **68**, 153 (1946).