The ultraviolet absorption spectra of the two forms show a displacement toward the visible of the absorption maximum of the *anti*-phenyl isomer (I).

No attempt has been made to convert one isomer into the other. Both forms are stable at room temperature and can be distilled unchanged under reduced pressure.

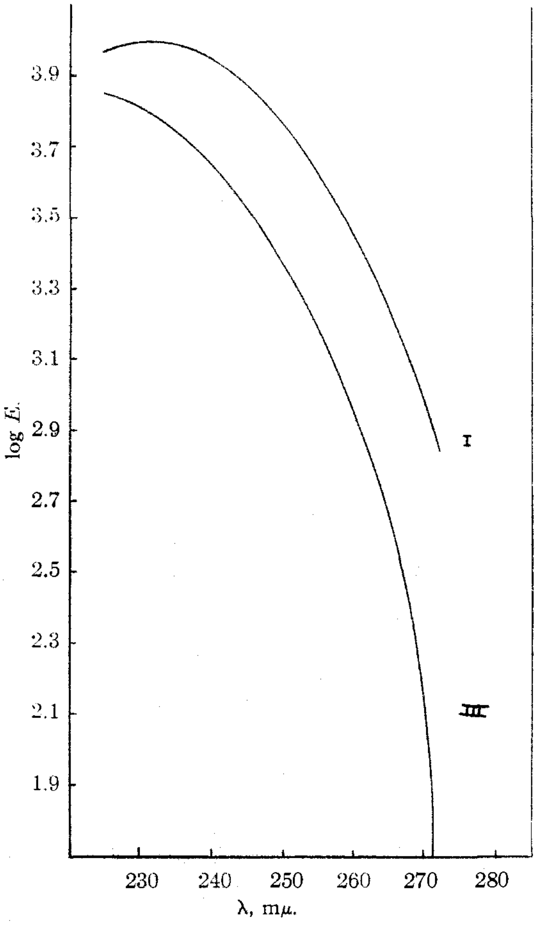

Fig. 1.—Absorption spectra of (I) *anti*-phenyl and (III) *syn*-phenyl isobutyrophenone oxime in 95% ethanol.

Experimental

Isobutyrophenone Oxime.—To a solution of 41.25 g. (0.28 mole) of isobutyrophenone in 125 cc. of absolute ethanol was added 28 g. of hydroxylamine hydrochloride and 41 g. of anhydrous sodium acetate. The mixture was refluxed for two hours and then filtered while hot. The filtrate was poured into 200 cc. of water and most of the alcohol was removed by distillation. The yellow oil which had separated solidified on cooling. It was filtered off and recrystallized from aqueous ethanol to yield 38 g. (83%) of a substance melting at 58–59.6°.

Separation of the Isomers.—When some of the above prepared oxime was dissolved in hot pentane and allowed to stand undisturbed for three days, there was formed a mixture of crystals. The large prisms were separated from the small plates by hand and recrystallized individually several times from pentane. Evaporation of the original mother liquor yielded more of the plate-like crystals. The less soluble form (prisms) melted at 95–96°, while the more soluble substance (plates) had a melting point of 89–90°. A mixture of the two melted somewhere between 57–60°, the exact melting point depending somewhat on the proportion of the two compounds.

Anal. Calcd. for $C_{10}H_{13}ON$: C, 73.59; H, 8.03. Found (prisms): C, 73.70; H, 8.01 (plates): C, 73.67; H, 8.25.

Cleavage of the Oximes.—Both forms of the oxime were cleaved with phthalic anhydride[5] to yield isobutyrophenone which was identified by its 2,4-dinitrophenylhydrazone derivative which melted at 161–162°. The reported[6] m. p. is 163°.

N-Isopropylbenzamide (IV).—To a stirred mixture of 42 g. of anhydrous potassium carbonate and 11 g. (0.2 mole) of isopropylamine in 180 cc. of ether was added, dropwise, 28 g. (0.2 mole) of benzoyl chloride over a period of forty minutes. The mixture was then stirred and refluxed for an additional hour after which it was added to 200 cc. of water and allowed to stand in a slow stream of air until all of the ether had evaporated. A white solid which had precipitated was filtered off, dried in air, and recrystallized from ethanol to give 29.3 g. (89%) of a substance which melted at 103–104°. After two recrystallizations from heptane the compound formed chunky needles which melted at 104–104.5°.

Anal. Calcd. for $C_{10}H_{13}ON$: C, 73.59; H, 8.03. Found: C, 73.70; H, 7.90.

Beckmann Rearrangement.—The method of Werner and Piguet[7] was used. A solution of 1.63 g. (0.01 mole) of the higher melting oxime in 20 cc. of dry pyridine was mixed with 1.8 g. of benzenesulfonyl chloride and was allowed to stand at room temperature for three hours. The orange solution was then poured into 125 cc. of 6 *N* H_2SO_4 and extracted with 250 cc. of ether. The ether extracts were dried over potassium carbonate and then evaporated to leave an oily residue which could be crystallized from hexane. After two crystallizations from that solvent, the material melted at 103–104° and weighed 0.76 g. (47%). Admixture of isobutyranilide (II) did not lower the melting point.

The rearrangement of 1.63 g. (0.01 mole) of the lower melting oxime was carried out as before with the exception that the pyridine solution was heated on the steam-bath for 30 minutes. There was obtained a solid which, after three recrystallizations from heptane weighed 0.53 g. (31%) and melted at 102–103°. When mixed with IV the substance melted at 103–104° but a mixture of the reaction product and II melted from 88–96°.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER, NEW YORK

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Error in the Average Coefficients of Specific Volume Change from 0 to 20° in Aqueous Solutions of Hydrogen Peroxide

BY FREDERICK G. KEYES AND CHARLES E. HUCKABA

It has come to our attention through the kindness of Professor W. F. K. Wynne-Jones of King's College, Newcastle-on-Tyne, England, that in a recent publication,[1] Tables VI and VII contain an anomaly due to the failure of equation 3 to reproduce the average coefficient of volume change in the specific volume of pure water between 0 and 20°. This involves also inaccuracies in the dilute solutions of peroxide. The revisions of Tables VI and VII are given below, based on a graph of the deviation of equation 3 from the experimental values of volume change, together

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[1] Charles E. Huckaba and Frederick G. Keyes, THIS JOURNAL, **70**, 2578 (1948).

with what appears to be the most reliable for pure water at 20°.

TABLE VI—REVISED

COMPARISON OF COMPUTED AND EXPERIMENTAL SPECIFIC VOLUMES

Weight fraction water	*v* exptl. at 20°	*v* calcd. at 20° Old table	New table
1.000	Lange 1.00180	1.00261	1.00186
	Dorsey 1.00184		
0.78475	0.92818	0.92826	.92816
.60841	.87037	.87006	.87023
.40917	.80836	.80836	.80853
.21471	.75103	.75101	.75103
.03123	.69888	.69918	.69904
.000	.....	.69068	.69053

TABLE VII—REVISED

AVERAGE COEFFICIENT OF SPECIFIC VOLUME CHANGE FROM 0–20° OF AQUEOUS SOLUTIONS OF HYDROGEN PEROXIDE AS A FUNCTION OF THE WEIGHT FRACTION OF WATER

The entries of the table are to be multiplied by 10^{-4}.

	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0	7.85	7.82	7.80	7.79	7.77	7.75	7.72	7.71	7.68	7.66
.1	7.65	7.62	7.60	7.58	7.55	7.53	7.50	7.48	7.45	7.42
.2	7.40	7.37	7.34	7.32	7.29	7.26	7.23	7.20	7.17	7.14
.3	7.11	7.08	7.05	7.02	6.98	6.95	6.92	6.88	6.85	6.81
.4	6.77	6.74	6.70	6.66	6.62	6.57	6.53	6.49	6.45	6.40
.5	6.36	6.31	6.26	6.21	6.16	6.11	6.05	6.00	5.94	5.88
.6	5.83	5.77	5.70	5.64	5.57	5.50	5.43	5.36	5.29	5.21
.7	5.14	5.06	4.97	4.88	4.79	4.70	4.61	4.51	4.41	4.31
.8	4.21	4.09	3.98	3.86	3.73	3.61	3.47	3.34	3.20	3.06
.9	2.92	2.74	2.56	2.37	2.18	1.97	1.76	1.54	1.31	1.07
1.0	0.83									

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASS.
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5,8-Dimethoxyquinoline[1]

BY C. E. KASLOW AND VERNON V. YOUNG[2]

It was desired to prepare 5,8-dimethoxyquinoline (III) in quantity for orientation studies and as the starting point in certain syntheses. 5,8-Dihydroxyquinoline has been reported in the literature. It was prepared by the alkali fusion of 8-hydroxy-5-quinolinesulfonic acid[3] and by the reduction of 5-nitroso-8-hydroxyquinoline[4] with iron and hydrochloric acid. Neither of these methods seemed to be feasible routes for the preparation of III. A series of dimethoxy-2,4-dimethylquinolines[5] has been prepared by condensation of acetylacetone with a dimethoxyaniline followed by ring closure in hot concentrated sulfuric acid. Since the Skraup reaction has been used with success in the preparation of 6,7-dimethoxyquinoline[6] from *p*-aminoveratrole and 7,8-dimethoxyquinoline[7] from *o*-aminoveratrole, it seemed the most direct route for the synthesis of III from 2,5-dimethoxyaniline. However, the Skraup reaction, with the usual modification of conditions, gave none of the desired product. Likewise the short-time Skraup reaction[8] as well as the modification[9] using acrolein failed to give III.

The alternate methods involved several steps starting either with ethyl ethoxalylacetate or with diethyl ethoxymethylenemalonate according to the general procedures described by Surrey and Hammer[10] and Price and Roberts,[11] respectively. Except for the availability of the esters, there was no advantage of one method over the other for the preparation of 5,8-dimethoxy-4-quinolinol (I). With ethyl ethoxalylacetate, the best results were obtained when one mole of the sodium salt was converted to the free ester, extracted with ether, dried and the ether removed by distillation then the crude ester used in the condensation reaction with 0.75 mole of 2,5-dimethoxyaniline Methylene dichloride was also used as an extractor for the ester, in which case it is only

TABLE I

SUBSTITUTED 5,8-DIMETHOXY-4-HYDROXYQUINOLINES

Compound	Formula	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
2-$CO_2C_2H_5$[a]	$C_{14}H_{15}NO_5$	146–147	5.06	5.01
2-CO_2H[b]	$C_{12}H_{11}NO_5$	215–216 (dec.)	5.62	5.57
3-$CO_2C_2H_5$[c]	$C_{14}H_{15}NO_5$	197–198	5.06	5.27
3-CO_2H[d]	$C_{12}H_{11}NO_5$	261–262 (dec.)	5.62	5.38

[a] Recrystallized from acetone, isopropyl alcohol or water. [b] Recrystallized from ethyl alcohol. [c] Recrystallized from acetone or isopropyl alcohol. [d] Recrystallized from ethyl alcohol.

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(1) Taken mainly from a thesis presented by Vernon V. Young in partial fulfillment of the requirements for the M. A. degree, August, 1947.

(2) Commercial Solvents Corporation, Terre Haute, Indiana.

(3) Claus and Posselt, *J. prakt. Chem.*, **41**, 40 (1890).

(4) Moness and Christiansen, *J. Am. Pharm. Assn.*, **23**, 228 (1934); Matsumura and Sone, THIS JOURNAL, **53**, 1406 (1931).

(5) Lions, Perkin and Robinson, *J. Chem. Soc.*, **127**, 1158 (1925).

(6) Frisch and Bogert, *J. Org. Chem.*, **9**, 338 (1944).

(7) Rajagopalan, *C. A.*, **35**, 7965 (1941).

(8) Elderfield, Gensler, Williamson, Griffing, Kupchan, Maynard, Kreysa and Wright, THIS JOURNAL, **68**, 1584 (1946).

(9) Bernstein and Yale, *ibid.*, **70**, 254 (1948).

(10) Surrey and Hammer, *ibid.*, **68**, 113 (1946).

(11) Price and Roberts, *ibid.*, **68**, 1204 (1946); "Organic Syntheses," Vol. 28, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 38.