Anal. Calcd. for $C_{13}H_{10}BrNO$: C, 56.5; H, 3.6. Found: C, 56.3; H, 3.9.

A solution of 0.5 g. of the amino ketone in 10 ml. of dilute hydrochloric acid was treated at 10° with 0.2 g. of sodium nitrite, allowed to stand for ten minutes, and then heated to boiling. The resulting 3-bromofluorenone separated from alcohol in the form of yellow plates (0.3 g.), m. p. 161–162°.

SCHOOL OF CHEMISTRY
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MINNEAPOLIS, MINNESOTA
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The Stereochemistry of Coördination Number Eight. Corrections

BY LOUIS E. MARCHI

Attention has been called to several serious errors which appeared in "The Stereochemistry of Coördination Number Eight."[1]

On page 331, in the right hand column, the sixth line from the bottom which reads 3AB CD EF should be deleted, since it is an obvious repetition of the line above it; the seventh line from the bottom should read 2AB CD EF instead of 3AB CD EF, since the latter is not a member of a class of coördination number eight.

In Table IV, page 332, the isomer numbers for Class AB, 6c, Configuration C, should be: Optically active, 0; Optically inactive, 1; Total, 1, instead of Optically active, 2; Optically inactive, 0; Total, 2. In the same table, on page 333, the isomer numbers for Class 3AB 2c, Configuration C, should be: Optically active, 14; Optically inactive, 2; Total, 16, instead of Optically active, 20; Optically inactive, 0; Total, 20.

(1) Marchi, THIS JOURNAL, **65**, 329–333 (1943).

MONSANTO CHEMICAL COMPANY
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The Reaction of Alkyl Halides with Potassium Iodide

BY H. J. MCDONALD, L. R. ROTHSTEIN AND H. E. ROBISON

Conant and Hussey[1] have previously described the reaction between several types of alkyl chlorides and potassium iodide. We have checked some of the results of these investigators and have extended their procedure to certain other alkyl halides.

We have found that there is no measurable reaction between either *t*-amyl chloride or *i*-butyl chloride and potassium iodide after contact times of twenty-four hours at temperatures up to 60°. The result obtained in the former case is not surprising in view of the fact that tertiary alkyl halides in general are extremely unreactive. In such second order substitution reactions, Conant[1] has shown the ease of substitution to be primary > secondary > tertiary.

On this basis it is difficult to see why the primary alkyl halide, *i*-butyl chloride, should prove so unreactive. For although the above-mentioned workers have also shown that branching of the chain reduces reactivity by as much as 100%, their data indicate that *i*-amyl chloride would have reacted with the iodide to an extent of 50% under the same conditions of time and temperature (twenty-four hours and 60°).

The possibility that the *i*-butyl compound might have rearranged during distillation to the more unreactive *t*-butyl chloride was eliminated by refractive index measurements; found, n^{25}_D 1.4000; known, n^{15}_D 1.40096.[2]

(1) Conant and Hussey, THIS JOURNAL, **47**, 476 (1925).

(2) Timmermans and Martin, *J. chim. phys.*, **23**, 747 (1926).

DEPARTMENT OF CHEMISTRY
ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO, ILLINOIS
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3,5-Diiodo-4-(4'-hydroxyphenoxy)-hippuric Acid and 3,5-Diiodo-4-(3',5'-diiodo-4'-hydroxyphenoxy)-hippuric Acid

BY CARL NIEMANN AND G. E. MCCASLAND

In the course of testing a series of reactions in order to determine their usefulness for the synthesis of thyroxine containing peptides 3,5-diiodo-4-(4'-hydroxyphenoxy)-hippuric acid and 3,5-diiodo-4-(3',5'-diiodo-4'-hydroxyphenoxy)-hippuric acid have been prepared and characterized.

3,5-Diiodo-4-(4'-acetoxyphenoxy)-benzoic Acid (I).—To 10 g. of recrystallized 3,5-diiodo-4-(4'-hydroxyphenoxy)-benzoic acid,[1] m. p. 259–60°, was added 40 ml. of acetic anhydride and 2–3 drops of concentrated sulfuric acid and the mixture heated at 100° for thirty minutes. The solution was cooled, poured into ice water and, after decomposition of the acetic anhydride, the colorless solid, which had separated, was collected, washed and dried *in vacuo*. The crude product (10.8 g.) was twice recrystallized from absolute ethanol to give 9.6 g. (89%) of I, colorless needles, m. p. 231–232°.

Anal. Calcd. for $C_{15}H_{10}O_5I_2$ (524): C, 34.4; H, 1.9; I, 48.4. Found: C, 34.7; H, 2.1; I, 48.8.

Ethyl 3,5-Diiodo-4-(4'-acetoxyphenoxy)-hippurate (II). To 3.1 g. of I suspended in 20 ml. of dry benzene was added 1.35 g. of phosphorus pentachloride and the mixture gradually heated to 70°. After cooling to 10° the crystalline acid chloride was collected, at 10°, and washed with 30–60° ligroin. The vacuum dried product weighed 2.7 g. A dry ethereal solution of glycine ethyl ester prepared by the method of Fischer[2] was standardized, by titration with standard acid, and the requisite amount of this solution added to the dry acid chloride and the mixture allowed to stand for sixteen hours at 5°. The solid was collected, washed several times with water and dried *in vacuo* to give 1.7 g. of II, colorless powder, m. p. 144–145°. The ethereal filtrate was washed with water, dilute hydrochloric acid, and again with water and dried first over anhydrous potassium carbonate and finally over Drierite. Evaporation of the dried solution gave an additional 0.7 g. of II for a total yield of 2.4 g. (67%).

Anal. Calcd. for $C_{19}H_{17}O_6NI_2$ (609): C, 37.5; H, 2.8; N, 2.3. Found: C, 37.5; H, 3.0; N, 2.4.

3,5-Diiodo-4-(4'-hydroxyphenoxy)-hippuric Acid Monohydrate (III).—To 2 g. of II was added 40 ml. of 1 *N* sodium hydroxide in 50% ethanol and the suspension

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(1) (a) C. R. Harington and G. Barger, *Biochem. J.*, **21**, 169 (1927); (b) C. Niemann and C. E. Redemann, THIS JOURNAL, **63**, 1549 (1941).

(2) E. Fischer, *Ber.*, **34**, 433 (1901).

stirred for three hours at 25°. The reaction mixture was filtered and the filtrate acidified with *N* hydrochloric acid. The precipitate was collected, washed, dried *in vacuo*, and recrystallized from 30% ethanol to give 1.7 g. (93%) of III, colorless needles, m. p. 186–187°.

Anal. Calcd. for $C_{15}H_{11}O_5NI_2 \cdot H_2O$ (557): C, 32.4; H, 2.4; N, 2.5. Found: C, 32.5; H, 2.7; N, 2.3.

3,5-Diiodo-4-(3′,5′-diiodo-4′-hydroxyphenoxy)-hippuric Acid (IV) —To 0.7 g. of III, dissolved in 10 ml. of 15·*N* ammonium hydroxide, was added, slowly and with stirring, the requisite amount of *N* potassium triiodide. When about half of the iodine had been added, the ammonium salt of IV separated in the form of glistening silvery leaflets. After all of the iodine had been added the solution was stirred for several minutes and allowed to stand at 5° for three to four hours. The suspension was decolorized with sodium metabisulfite and the free acid liberated by the addition of acetic acid. The precipitate was collected, washed with water, and dried *in vacuo* to give 1.0 g. (97%) of IV, colorless crystalline powder, m. p. 248° with decomposition and evolution of iodine. After recrystallization from 70% ethanol IV was obtained as colorless leaflets, m. p. 248° with decomposition.

Anal. Calcd. for $C_{15}H_9O_5NI_4$ (791): C, 22.8; H, 1.1; N, 1.8. Found: C, 22.8; H, 1.5; N, 1.8.

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GATES AND CRELLIN LABORATORIES OF CHEMISTRY
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The Light Absorption and Fluorescence of Triarylmethyl Free Radicals

BY LINUS PAULING

By working at low temperatures with triarylmethyl free radicals frozen in a rigid glassy solvent, Lewis, Lipkin, and Magel[1] have obtained absorption spectra and fluorescence spectra which show a striking vibrational fine structure, essentially the same for absorption (determined by the vibrational structure of the excited state) and fluorescence (determined by the normal state); the authors report nine vibrational frequencies for the triphenylmethyl radical, and their reproduced microphotometer records indicate one or two more (Table I).

TABLE I

COMPARISON OF VIBRATIONAL FREQUENCIES

Triphenylmethyl		Benzaldehyde
Absorption	Fluorescence	Raman
190	230	239 cm^{-1}.
(400)[a]		439
600	670	615
820		827
970	970	1001
1090	1080	1164
		1203
1520	1550	1597
	1850	
	2210	
	2510	
		3063

[a] Estimated from the published microphotometer record.

It may be noted that an interesting correlation exists between these absorption and fluorescence spectra of triphenylmethyl and the Raman spectra of substituted benzenes. The principal Raman frequencies of substituted benzenes are 200, 400, 615, 1000, 1165, 1595, and 3060 $cm.^{-1}$; all but the last (the carbon–hydrogen stretching frequency) are represented in the absorption and fluorescence spectra. The correlation is closest with monosubstituted benzenes containing a group conjugated with the benzene ring, such as methyl benzoate and benzaldehyde; Raman frequencies for benzaldehyde (other than the carbonyl frequency 1700 $cm.^{-1}$) are given for comparison in Table I. There is a rough correlation in intensity as well as in frequency.

The bands at 1850, 2210, and 2510 may be combinations or overtones; they may well be combinations of the important frequency 1550 $cm.^{-1}$ with lower frequencies. The failure of the band with shift 3063 $cm.^{-1}$ to appear in the fluorescence spectrum may indicate that the coupling of this C–H vibration with the electronic transition is very weak.

An interesting detail is the gradual change in shape of the absorption spectrum in the 1000–1200 $cm.^{-1}$ region as the phenyl groups in the triphenylmethyl radical are successively replaced by *p*-*t*-butylphenyl groups. The band at 1000 $cm.^{-1}$ gradually diminishes in intensity, and finally disappears; the spectrum of tri-(*p*-*t*-butylphenyl) methyl, which otherwise closely resembles that of triphenylmethyl, shows a single peak at 1120 $cm.^{-1}$ in place of the 970–1080 doublet. This fact is without doubt related to the observed characteristic absence of the lines near 1000 $cm.^{-1}$ in the Raman spectra of the para-disubstituted benzenes.

I believe that measurements of well-resolved absorption spectra, fluorescence spectra, and phosphorescence spectra of rigid solutions at low temperatures may provide much useful information about the vibrational frequencies of molecules of dyes and other substances which could not be readily obtained by the techniques of Raman and infrared spectroscopy.

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[1] G. N. Lewis, D. Lipkin, and T. T. Magel, THIS JOURNAL, 66, 1579 (1944).

The System Sodium Molybdate–Sodium Nitrate–Water and Part of the System Sodium Molybdate–Molybdic Oxide–Water, at 25°

BY J. E. RICCI AND L. DOPPELT[1]

The experimental procedure for these measurements was that described for similar investigations of ternary systems of salts and water. The materials used were C. P. products throughout, the molybdic oxide being a very pure sample,[2] found

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[1] Present address: U. S. Army.

[2] This material, resublimed and of stated purity 99.97%, was the gift of the Climax Molybdenum Company.