in the methyl substituted 8-quinolinols is the failure of 2-methyl, 2,3-dimethyl, 2,4-dimethyl and 2,3,4-trimethyl-8-quinolinol to precipitate aluminum.

TABLE I

ACIDIC AND BASIC IONIZATION CONSTANTS OF 8-QUINOLINOLS

Substituent	$K_b \times 10^{10}$	$K_a \times 10^{10}$
None[1]	8.32	1.95
3-CH_3	8.71	1.78
2-CH_3[6]	35.5	0.490
4-CH_3[6]	36.4	1.00
$3,4\text{-(CH}_3)_2$[6]	63.1	0.892
$2,3\text{-(CH}_3)_2$	74.1	.630
$2,4\text{-(CH}_3)_2$[6]	159	.252

The ultraviolet absorption spectra of these compounds in acid and base are very similar to 8-quinolinol[8,9] (Table II). The longest wave length of maximum absorption in both acid and base is shortened by the presence of a 2-methyl group and the molecular extinction at this band is highest for the compounds containing a 4-methyl group.

TABLE II

ABSORPTION MAXIMA IN ULTRAVIOLET SPECTRA OF METHYL-8-QUINOLINOLS[a]

Substituent	mμ	mμ	mμ
	A, in 0.1 *N* hydrochloric acid		
2-CH_3[3]	255(44000)	320(3100)	345(1700)
3-CH_3	254(45000)	320(2300)	355(1900)
4-CH_3[3]	250(44000)	315–318(1700)	350–353(2400)
$2,3\text{-(CH}_3)_2$	255(45000)	323(3700)	342(1900)
$2,4\text{-(CH}_3)_2$[3]	252(48000)	318(3100)	342(2400)
$3,4\text{-(CH}_3)_2$	252(40000)	318(2100)	353(2500)
$2,3,4\text{-(CH}_3)_3$	255(44000)	316(2500)	346–349(2600)
	B, in 0.1 *N* sodium hydroxide		
2-CH_3[3]	255(30000)		335(3000)
3-CH_3	256–257(30000)		355(2700)
4-CH_3[3]	253(28000)		343(3900)
$2,3\text{-(CH}_3)_2$	257(37000)		335(3300)
$2,4\text{-(CH}_3)_2$[3]	255(31000)		337(4200)
$3,4\text{-(CH}_3)_2$	255(35000)		350–353(3800)
$2,3,4\text{-(CH}_3)_3$	255(41000)		340–345(4200)

[a] Figures in parentheses are molecular extinctions.

The solubilities of the methyl-8-quinolinols are with the exception of 8-hydroxyquinaldine very low: for example, a saturated solution of 3-methyl-8-quinolinol has a molarity of 5.4×10^{-4}, of 2,3-dimethyl-8-quinolinol a molarity of 4.8×10^{-4}, as compared to 2.67×10^{-3} for 8-hydroxyquinaldine.

Attempts to correlate various properties of methyl substituted 8-quinolinols with their formation of metal chelates led to the following generalizations: (1) The presence of a group in the 2-position is sufficient to prevent aluminum from forming an insoluble chelate.[2,3] (2) The lower the *p*H at which a metal is precipitated the more insoluble the metal chelate is; this is the same relation observed in the precipitation of metals as hydroxides by ammonia.[10] (3) There appears to be no simple relation between ionic radii of metals and their conditions of chelate formation with 8-quinolinols. (4) The more basic (and less acidic) substituted 8-quinolinols precipitate metal chelates at higher *p*H values.[3]

Acknowledgment.—The author is grateful to the Research Corporation for a grant in support of this work.

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(8) Ewing and Steck, THIS JOURNAL, **68**, 2181 (1946).

(9) Phillips, Huber, Chung and Merritt, *ibid.*, **73**, 630 (1951).

(10) Phillips and Price, *ibid.*, **73**, 4414 (1951).

LOUISVILLE, KENTUCKY RECEIVED JUNE 29, 1951

NOTES

Manometric Estimation of Citric Acid

BY SAMUEL J. AJL, DONALD T. O. WONG AND DAVID F. HERSEY

A number of methods, enzymatic and chemical, have been described for the determination of small amounts of citric acid. Of the chemical methods, the majority involve the conversion of citric acid to pentabromoacetone, which may be estimated by various gravimetric, titrimetric or colorimetric procedures. The recent modifications[1-3] of this method have simplified it and increased the sensitivity. However, even in the simplified methods, the procedures are quite laborious. The method described in this communication is considerably faster and simpler to carry out.

Citric acid (14–400 micrograms) is oxidized manometrically under controlled conditions with ceric sulfate; the CO_2 produced is a measure of citric acid concentration.

Procedure

Manometric Estimation of Citric Acid.—Warburg flasks of about 20-ml. capacity with or without a center well and a side-arm of 1-ml. capacity are usually employed. The citric acid solution, usually 1 ml., is added to the main compartment. 0.5 ml. of 6 *N* H_2SO_4 is next pipetted into the main compartment to liberate all of the bound CO_2. 0.4 ml. of saturated ceric sulfate (a saturated solution is prepared by heating on a steam-bath an excess of the compound in 4 *N* H_2SO_4 for 6 to 12 hours with occasional stirring) is added to the side-arm. The control vessel is made up in the same way, excepting that 1 ml. of distilled water is placed in the main compartment, in place of the citric acid solution. The bath temperature is adjusted to 30°. After a 10-minute shaking period with the stopcocks open for equilibration, the manometric fluid is adjusted so as to provide a maximum scale for reading and the stopcocks are closed. If equilibration is attained, the content of the side-arm is delivered into the main compartment and the manometers quickly replaced on the bath. Readings are then taken every two or three minutes until the delta values (CO_2 evolution per unit time) of the control and the experimental manometers are equal on two successive readings. The reaction is usually complete in less than 10 minutes.

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(1) H. H. Taussky and E. Shorr, *J. Biol. Chem.*, **169**, 103 (1947).

(2) S. Natelson, J. K. Luguvoy and J. B. Pincus, *ibid.*, **170**, 597 (1947).

(3) G. H. Wolcott and P. D. Boyer, *ibid.*, **172**, 729 (1948).

Determination of Citric Acid in the Presence of Interfering Substances.—It is usually necessary to estimate citric acid in the presence of one or more Krebs cycle intermediates. The substances which yield CO_2 when oxidized with ceric sulfate are α-ketoglutaric acid, pyruvic acid, oxalacetic acid, and, to some extent, malic acid. (All of the compounds mentioned, with the exception of malic acid, could actually be determined with ceric sulfate. For each mole of α-ketoglutarate, one mole of CO_2 and one mole of succinate is formed; for each mole of pyruvic acid, one mole of CO_2 and one mole of acetic acid is formed, and for each mole of oxalacetic acid, two moles of CO_2 are formed and one mole of acetic acid.) Fumarate, acetate, succinate and *cis*-aconitate do not interfere. When interfering substances are present, it is best to ether extract the deproteinated sample and isolate the citric acid by paper chromatography.[4] Citrate is stable and partitions well between *t*-amyl alcohol, formic acid and water. The citric acid spot is eluted with boiling water and quantitatively estimated manometrically, as indicated above.

Determination of Citrate in Biological Material.—Typical results are shown in Table I: 1, 5 and 10 mg. of known citric acid were added to three different flasks, each of which contained 3 ml. of a dialyzed cell-free extract of *Escherichia coli*, prepared according to the method of Utter, *et al.*[5] The extract was subsequently deproteinated, ether-extracted and appropriate dilutions thereof chromatographed. The eluted citrate bands were boiled down and the quantities determined manometrically with ceric sulfate. Recoveries ranged between 104 and 98.6%.

TABLE I

DETERMINATION OF CITRIC ACID IN BACTERIAL CELL-FREE EXTRACTS

Sample No.	Citric acid added, mg.	Citric acid recovered, mg.	Recovered, %
1	1	1.04	104
2	5	4.93	98.6
3	10	10.00	100

Analytical Range.—The smallest quantity of citric acid which can be determined by the manometric method is limited chiefly by the accuracy of the manometric equipment. Since 14 γ of citric acid is equivalent to $\sim$ 5 μl. of CO_2, this amount can be considered the lower limit of the method. The upper limit of this method depends upon the concentration of ceric sulfate. For routine work, 0.5 ml. of saturated ceric sulfate is enough to determine 400 γ of citric acid.

Discussion

The data in Fig. 1 show that a linear relationship was found between microliters of CO_2 liberated and micromoles of citric acid present up to a level of 2.08 micromoles (400 micrograms) of citric acid. Three micromoles of CO_2 were obtained for each mole of citrate oxidized, in accordance with the probable equation for the oxidation.

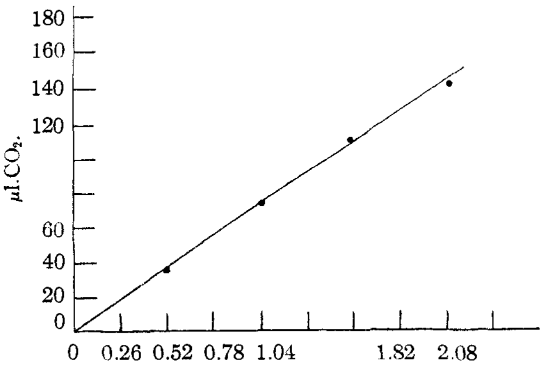
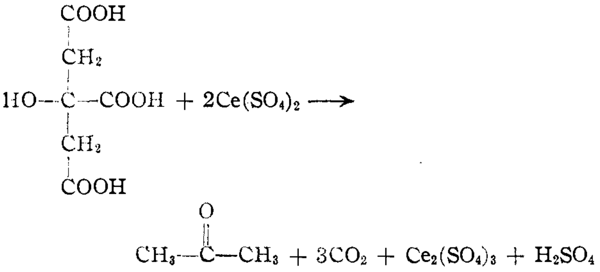


Fig. 1.—Manometric estimation of citric acid with ceric sulfate.



$$\begin{array}{l} \mathrm{COOH}\\ \;|\\ \mathrm{CH_2}\\ \;|\\ \mathrm{HO{-}C{-}COOH} + 2\mathrm{Ce(SO_4)_2} \longrightarrow\\ \;|\\ \mathrm{CH_2}\\ \;|\\ \mathrm{COOH}\end{array}$$

$$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_3} + 3\mathrm{CO_2} + \mathrm{Ce_2(SO_4)_3} + \mathrm{H_2SO_4}$$

It is for this reason that during the determination of citric acid a standard curve need not be constructed. If one divides by three the number of microliters of CO_2 given off during citric acid oxidation, one immediately obtains the number of micromoles of citric acid present.

DEPARTMENT OF BACTERIOLOGY AND IMMUNOLOGY
WASHINGTON UNIVERSITY MEDICAL SCHOOL
ST. LOUIS, MISSOURI
RECEIVED MAY 7, 1951

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(4) J. W. H. Lugg and B. T. Overell, *Austral. J. Sci. Res.*, **1**, 98 (1948).

(5) M. F. Utter, G. Kalnitsky and C. H. Werkman, *J. Bact.*, **49**, 595 (1945).

A Convenient Synthesis of Orthoformic Esters

BY ELLIOT R. ALEXANDER[1] AND HIRSH M. BUSCH[2]

One of the best known syntheses for orthoformates involves the reaction of an alkoxide with a haloform

$$3\mathrm{RONa} + \mathrm{HCX_3} \longrightarrow \mathrm{HC(OR)_3} + 3\mathrm{NaX} \quad (1)$$

Thus, as early as 1854, ethyl orthoformate was prepared in this manner by Williamson and Kay.[3] Since its discovery the method has been used for the preparation of methyl,[4] propyl,[4] isobutyl,[4] isoamyl,[5] phenyl,[5] allyl,[6] *o*-nitrophenyl,[7] *n*-butyl[8] and isopropyl[8] orthoformates. The yields, however, usually range from 20 to 50%.

Although there is another method for the preparation of orthoesters,[9] it seemed possible that a general procedure could be developed based upon an ester interchange with ethyl orthoformate. It is known that ethyl orthoformate and propyl alcohol give an equilibrium mixture of ethyl orthoformate, *n*-propyl diethyl orthoformate, di-*n*-propyl ethyl orthoformate, *n*-propyl orthoformate and ethyl alcohol.[10] Hence, it seemed possible to obtain the pure alkyl orthoformate by removing the ethyl alcohol as it was formed and thereby displacing the equilibrium to the right (2).

$$\mathrm{HC(OC_2H_5)_3} + 3n\text{-}\mathrm{C_3H_7OH} \rightleftarrows \mathrm{HC(OC_3H_7)_3} + 3\mathrm{C_2H_5OH} \quad (2)$$

Although this possibility does not seem to have been investigated as a general method, it is interesting

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(1) Deceased.

(2) University of Illinois, College of Dentistry, Chicago, Illinois.

(3) A. W. Williamson and G. Kay, *Ann.*, **92**, 346 (1854).

(4) A. Deutch, *Ber.*, **12**, 115 (1879).

(5) F. Tiemann, *ibid.*, **15**, 2686 (1882).

(6) F. F. Beilstein and E. Wiegand, *ibid.*, **18**, 482 (1885).

(7) A. Weddige, *J. prakt. chem.*, [2] **26**, 444 (1882).

(8) P. P. T. Sah and T. S. Ma, THIS JOURNAL, **54**, 2965 (1932).

(9) A. Pinner, *Ber.*, **16**, 352 (1883); *ibid.*, **16**, 1643 (1883).

(10) W. H. Post and E. R. Erickson, THIS JOURNAL, **55**, 3851 (1933).

TABLE I

Compound ortho-formate	Yield, %	Empirical formula	B.p. °C.	B.p. Mm.	d^{20}_4	n^{20}_D	Analyses, % MR Calcd.	MR Found	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
n-Propyl	95.3	$C_{10}H_{22}O_3$	96–97	20	0.8830	1.4078	53.51	53.21				
n-Butyl	86.3	$C_{13}H_{28}O_3$	141	25	.8682	1.4184	67.18	67.34				
Isobutyl	86.0	$C_{13}H_{28}O_3$	118–120	22	.8584	1.4122	67.18	67.23				
s-Butyl[b]	87.5	$C_{13}H_{28}O_3$	115	23	.8632	1.4141	67.18	67.27	69.19	96.05	12.14	12.27
n-Amyl[b]	74.0	$C_{16}H_{34}O_3$	101–103	0.3	.8714	1.4290	81.02	81.17	70.03	69.99	12.48	12.23
Isoamyl	88.2	$C_{16}H_{34}O_3$	81–83	0.3	.8632	1.4251	81.02	81.14				
n-Hexyl[b]	77.4	$C_{19}H_{40}O_3$	127–128	0.35	.8621	1.4344	94.90	95.66	72.07	71.99	12.74	12.75
Benzyl[b]	[a]	$C_{22}H_{22}O_3$	.....	...	....	1.5645			79.01	78.93	6.63	6.84

[a] Yield was not calculated because attempted distillation decomposed some of the product obtained. [b] New compound.

that several high boiling orthoformates (*l*-menthyl,[11] bornyl[11] and *s*-octyl[12]) have been prepared in this manner.

The modified method of Mkitaryan and Hunter was applied to the preparation of seven orthoformates with yields ranging from 74 to 95%. Experiments were also carried out for the preparation of isopropyl and *t*-butyl orthoformates but in each case the interchange did not occur. The preparation of allyl orthoformate led to a mixture of products that could not be separated by distillation. Benzyl and *n*-octyl orthoformates decomposed on distillation at 0.3 mm. pressure, but the benzyl orthoformate was found to crystallize in cold storage (4 to 10°), m.p. about 8°.

Experimental[13]

In all cases the ethyl orthoformate and the alcohols employed were distilled to constant refractive index before use.

The experiments summarized in Table I were carried out according to the following procedure. It is illustrated here with the preparation of *s*-butyl orthoformate.

***s*-Butyl Orthoformate.**—To a 500-ml. flask was added 74.1 g. (0.5 mole) of ethyl orthoformate and 128.2 g. (2.0 moles) of *s*-butyl alcohol. A "Thermocap" was used and adjusted so that a maximum temperature of the condensing vapor was 79° by controlling the heat to the flask. The mixture was heated for 24 hours (removing the ethyl alcohol as it was formed) and the vapor rectified through a fourteen inch column packed with glass helices. Upon removal of the theoretical amount of ethyl alcohol (69.0 g., 1.5 moles), the mixture was distilled under vacuum. *s*-Butyl orthoformate was obtained as a colorless liquid (see Table I).

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(11) V. G. Mkitaryan, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 1361 (1938); *C. A.*, **33**, 4222 (1939).

(12) H. Hunter, *J. Chem. Soc.*, **125**, 1389 (1924).

(13) All boiling points are uncorrected.

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RECEIVED AUGUST 27, 1951

Reactions of Nitrous Acid

BY A. T. AUSTIN, E. D. HUGHES, C. K. INGOLD AND J. H. RIDD

It was shown by T. W. J. Taylor, for the aqueous deamination of primary aliphatic amines by nitrous acid,[1] that the reaction rate has the form

$$\text{Rate} \propto [\text{amine}][\text{HNO}_2]^2$$

where [amine] means the concentration of free amine, and $[HNO_2]$ that of undissociated acid, this specification taking adequate care of the dependence of the rate on *p*H; the equation can be put into other forms, because kinetics cannot locate rapidly transferable protons. Taylor observed the same kinetic law for the formation of nitrosamines from aliphatic secondary amines.[2] Abel and his co-workers obtained it again for the reaction of ammonia with nitrous acid.[3] Schmid and Muhr obtained it yet again for the diazotization of aromatic primary amines.[4] The implication is that it is a kinetic law for rate-controlling N-nitrosation.

Of the various interpretations which have been suggested, that of Hammett[5] has been proved to be correct.[6] It is simply that the active nitrosating agent in mildly acidic aqueous conditions is dinitrogen trioxide.

Papers by Dusenbury and Powell have just appeared[7] in which the opinion is expressed that Taylor's rate law is erroneous, and, in particular, that the second ("unnecessary") molecule of nitrous acid which it involves is "non-existent." They do not state that they have repeated Taylor's work. Now it happens that we have repeated nearly the whole of it, and we therefore feel it encumbent on us to report that we have found it to be entirely accurate.

For ammonia and methylamine Dusenbury and Powell observed the rate law

$$\text{Rate} \propto [\text{amine}][\text{HNO}_2][\text{H}^+]$$

But they were working in phosphate buffers; they could have been replacing the usual nitrosating agent, dinitrogen trioxide, by a nitrosyl phosphate, or even in part by nitrosyl chloride when sodium chloride was added to make up the ionic strength. Any such nitrosyl compound of an anion present in excess, if acting as the deaminating agent, could lead to the observed rate law, as also could the nitrous acidium ion, or the nitrosonium ion. The observed law, without other information, does not diagnose mechanism. Schmidt and Muhr's work indicated the presence of a reaction of amines with nitrosyl chloride. We may mention that we have shown that nitrosyl bromide, and also the nitrous acidium ion, can replace the usual dinitrogen trioxide as nitrosating agent in buffer solutions not very dissimilar to those of Dusen-

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(1) T. W. J. Taylor, *J. Chem. Soc.*, 1099, 1897 (1928).

(2) T. W. J. Taylor and L. S. Price, *ibid.*, 2052 (1929).

(3) E. Abel, H. Schmid and J. Schafranik, *Z. physik. Chem.*, Bodenstein Festband, 510 (1931).

(4) H. Schmid and G. Muhr, *Ber.*, **70**, 421 (1937).

(5) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 294.

(6) E. D. Hughes, C. K. Ingold and J. H. Ridd, *Nature*, **166**, 642 (1950); A. T. Austin, E. D. Hughes, and C. K. Ingold, forthcoming paper.

(7) J. H. Dusenbury and R. E. Powell, THIS JOURNAL, **73**, 3266, 3269 (1951).

bury and Powell. For these reasons we do not doubt either the results of T. W. J. Taylor, or those of Dusenbury and Powell.

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W.C.1, LONDON, ENGLAND RECEIVED SEPTEMBER 18, 1951

Chemistry of Technetium. I. Preparation of Technetium Heptoxide

BY G. E. BOYD, J. W. COBBLE, C. M. NELSON AND W. T. SMITH, JR.[1]

In the study of the chemistry of technetium it was necessary to establish the formula of the compound formed on heating the element in dry oxygen at 400–600°. Fried and co-workers[2] have suggested the product of this reaction may be TcO_3. However, elemental rhenium, when burned under these conditions gives Re_2O_7.[3] We were first led to the view that the oxidation product in reality was Tc_2O_7 by the observation that the titer of a standardized Ce(IV) solution was not changed upon adding milligram quantities of the compound. Furthermore, the absorption spectrum (Fig. 1) of an aqueous solution of the oxide was found to be identical before and after its treatment with alkaline H_2O_2 suggesting that the technetium was already Tc(VII).

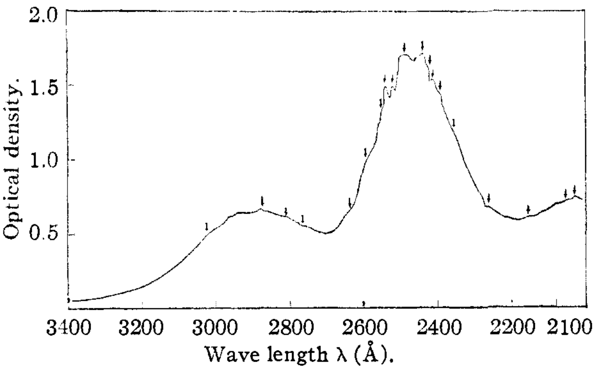

Fig. 1.—Ultraviolet absorption spectra of 3×10^{-4} *M* NH_4TcO_4 *vs.* H_2O at 25° determined with Beckman model DU spectrophotometer using variable slit width and constant sensitivity; source: H_2 discharge lamp. Molar extinction coefficient at 2470 Å. = 4000.

Quantities of technetium metal[4] were burned and the light yellow crystalline oxide (m.p. 119.5 ± 0.1°) formed was purified by repeated sublimations into cooler portions of the quartz reaction tube. An aqueous solution containing a known quantity of the compound was prepared by sealing off an aliquot in a small quartz tube, weighing and breaking the same, and then reweighing its parts after the oxide had dissolved completely. The oxide, which is very hygroscopic, dissolved to give a pink solution whose color disappeared with dilution. A potentiometric *p*H titration was performed using 0.05 *f* ammonium hydroxide. The titration curve, which was characteristic of a strong monobasic acid, showed but one inflection point. The entire neutralized solution was taken to dryness in a platinum dish at 95° and the weight of technetium salt was determined. Pure NH_4TcO_4 is nonhygroscopic and shows no decomposition when kept in air at 100° for several hours. Analytical results from two experiments are given in Table I where a comparison with the titers for Tc_2O_7 and TcO_3, respectively, is made.

TABLE I

EVIDENCE THAT THE FORMULA OF THE YELLOW OXIDE OF TECHNETIUM IS Tc_2O_7

Wt. of oxide, mg.	Millimoles[a] as Tc_2O_7	M.e. as Tc_2O_7	Millimoles as TcO_3	M.e. as TcO_3	M.e. OH^- required	M.e. NH_4TcO_4 found
157.7	0.5087	1.017	1.073	2.146	1.019	1.020
70.11	0.2262	0.4524	0.4769	0.9538	0.4561	0.4564

[a] The theoretical isotopic weight of 99.0 given by Metropolis and Reitinuiner (NP-1980, USAEC, March, 1950) was used in the calculations. Although fission product Tc^{99} may contain small quantities of other isotopes, the amounts will be such as to give a negligible error.

It was concluded that the correct formula for the light yellow oxide produced by heating technetium metal in dry oxygen at 400–600° is Tc_2O_7.

The intense ultraviolet absorption (Fig. 1) of pertechnetate ion in aqueous solutions may be employed for the spectrophotometric determination of Tc(VII). Beer's law was found to hold rather well up to concentrations of 10^{-3} *M* for wave lengths near both maxima (*i.e.*, 2470 and 2890 Å.). As little as 10^{-8} g. of technetium may be detected, which sensitivity compares quite favorably with that obtained spectrochemically.[5] A third absorption band in the far ultraviolet in addition to those previously measured[2] at longer wave lengths is suggested (Fig. 1).

Previously,[6] relatively concentrated strongly acid technetium solutions had been found to show a pink coloration. In this work when a 1 *M* aqueous solution of Tc_2O_7 was slowly evaporated at room temperature over concentrated sulfuric acid, it became yellow, dark yellow, red and dark red; finally, long red-black crystals formed. These hygroscopic crystals were rapidly weighed (15 seconds) and then were allowed to absorb water from the atmosphere to form a dark red solution.

TABLE II

FORMULA OF RED-BLACK CRYSTALS RESULTING FROM THE ISOTHERMAL EVAPORATION OF AQUEOUS Tc_2O_7 SOLUTIONS

Tc_2O_7 hydrate, mg.	Weight of NH_4TcO_4 formed, mg.	Mol. wt. of hydrate	Hydrate formula
1st weighing, 98.1	108.5	327.4	$Tc_2O_7(H_2O)_{0.97}$
2nd weighing, 98.5	...	328.6	$Tc_2O_7(H_2O)_{1.03}$

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(1) Department of Chemistry, University of Tennessee, Knoxville, Tenn.

(2) S. Fried, A. H. Jaffey, N. F. Hall and L. E. Glendenin, *Phys. Rev.*, **81**, 741 (1951).

(3) A. D. Melaven, J. N. Fowle, W. Brickell and C. F. Hiskey, "Inorganic Syntheses," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 188.

(4) The pure metal was produced from technetium separated from a "crude" tetraphenylarsonium perchlorate + pertechnetate precipitate dissolved in concentrated H_2SO_4 kindly supplied to us by G. W. Parker, leader of the "hot" laboratory group, Chemistry Division, ORNL. The details of the preparation will be reported in another communication.

(5) D. Timma, *J. Optical Soc.*, **39**, 898 (1949).

(6) E. E. Motta, G. E. Boyd and Q. V. Larson, *Phys. Rev.*, **72**, 1270 (1947).

A second evaporation and weighing was conducted after which the technetium was converted to NH_4TcO_4 and weighed. It appears (Table II) that the dark red crystals formed on evaporating aqueous solutions of Tc_2O_7 correspond to $Tc_2O_7 \cdot H_2O$, or to anhydrous pertechnic acid, $HTcO_4$.

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RECEIVED SEPTEMBER 28, 1951

The Solubility of Bismuth in Mixtures of Bismuth Chloride with Other Chlorides

BY GEORGE CLEARY[1a] AND DANIEL CUBICCIOTTI[1b]

The solubility of cadmium in cadmium chloride has been shown to be greatly influenced by the addition of other chlorides.[2] The properties of the added salt that appeared to determine its effect on the solubility of the cadmium were the anion-to-cation ratio and the electropositiveness of the metal of the cation. The present study on bismuth was made parallel to that on cadmium to investigate the influence of added salt.

Experimental

Method.—The method was similar to that used in the cadmium system.[2] Mixtures of about 10 g. of salt and 10 g. of metal were sealed into iron tubes by brazing with a high melting brazing alloy. The mixtures were equilibrated at 450° for one hour, quenched in water, and samples of the salt phase taken for analysis. These weighed samples of salt were leached with concentrated hydrochloric acid, which dissolved the salts and left a precipitate of the bismuth metal that had been dissolved in the salt. The bismuth precipitate was dissolved in concentrated nitric acid and then precipitated as BiOCl after the proper adjustment of the acidity and chloride concentration of the solution. The oxychloride was dried and weighed, and the composition of the salt phase calculated from its weight together with the weight of the sample and the original salt composition.

Materials.—Anhydrous bismuth trichloride was obtained from the J. T. Baker Co. The other anhydrous salts were prepared by heating the hydrate or the moist salt *in vacuo*.

Results and Discussion

Two separate determinations of the solubility of bismuth in its chloride gave 47.3 and 47.8 mole per cent. bismuth in the final mixture at 450°. This compares favorably with the value of 46.6 mole per cent. given by Eggink[3] at 320°.

The effect of added salts on the solubility of the bismuth is shown in Fig. 1. It may be seen from the figure that cuprous chloride reduces the solubility more than zinc chloride and sodium chloride more than calcium chloride. Thus with salts of metals of about the same electropositiveness, the larger the anion to cation ratio, the less effective the salt in reducing the solubility of the metal. It can also be seen that sodium chloride reduces the solubility more than cuprous chloride and calcium chloride more than zinc chloride. For salts of the same anion to cation ratio, the more electropositive the metal of the cation, the more effective the salt in reducing the solubility.

These results are in accord with the data observed in the case of cadmium[2] and fit the hypothesis suggested concerning the structure of metal-in-salt solutions.

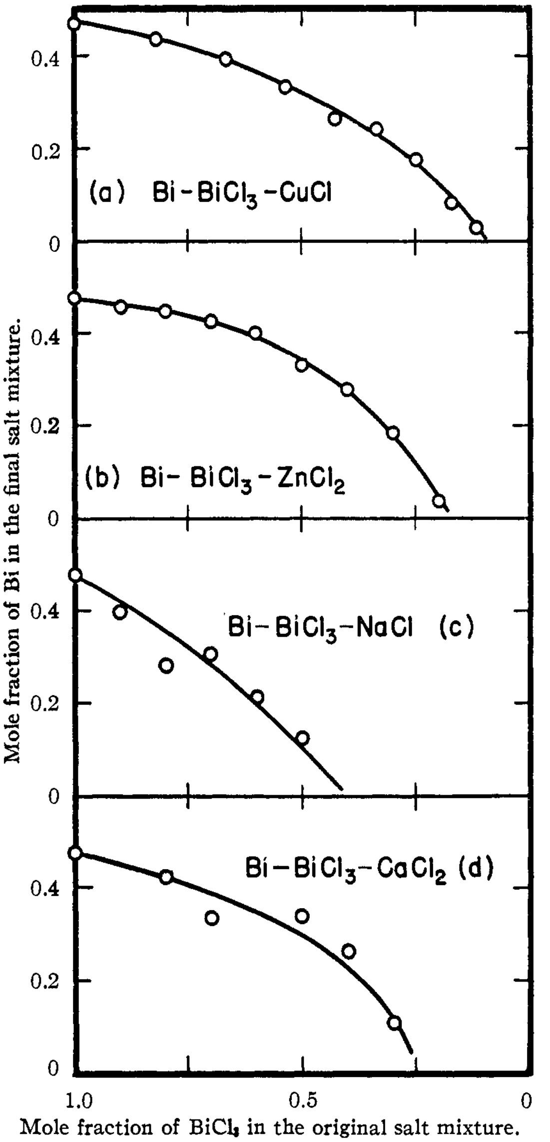

Fig. 1.—Influence of added salt on the solubility of bismuth in its trichloride at 450°.

Acknowledgment.—The authors are grateful to the Office of Naval Research for their support of this work.

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(1) (a) Sinclair Research Laboratories, Harvey, Illinois. (b) North American Aviation, Inc., Downey, Calif.

(2) D. Cubicciotti, THIS JOURNAL, to be published.

(3) Eggink, *Z. physik. Chem.*, **64**, 493 (1908).

The Oxidation of Calcium at Elevated Temperatures

BY DANIEL CUBICCIOTTI[1]

The ratio of molal volumes of calcium oxide to calcium metal is about 0.95. Since the ratio was less than unity, Pilling and Bedworth[2] expected the metal to oxidize according to the linear law. In their experiments, of long duration, the metal did oxidize linearly.

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(1) North American Aviation, Inc., Downey, Calif.

(2) N. B. Pilling and R. E. Bedworth, *J. Inst. Metals*, **29**, 529 (1923).

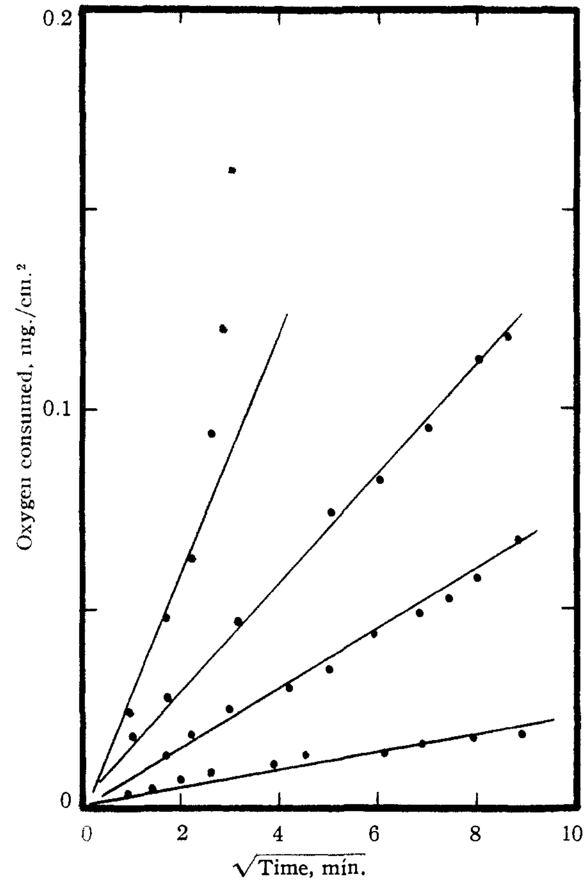

Fig. 1.—The oxidation of calcium at 330, 350, 385 and 435°; parabolic plot.

The oxide that forms initially is dark colored and appears to adhere to the metal. For that reason and because the ratio of volumes of oxide to metal is so close to unity the author felt that the initial portion of the oxidation curve might be parabolic. The present study shows that such is the case.

Experimental

The method was the same as that used previously in this Laboratory.[3] For the rapid oxidations a 500-cc. bulb was added to the system outside the furnace. The sample was a cube approximately 1 cm. on edge of electrolytic calcium, 99% pure, obtained from the A. D. Mackay Co., New York. Before each oxidation, the sample was abraded under carbon tetrachloride with 2/0 emery paper. The samples were heated for 100 min. *in vacuo* before oxygen was admitted to start the reaction.

Results and Discussion

The oxidation was studied for 100 min. from 330 to 475° at 20 cm. oxygen pressure. Typical oxidation curves are shown in Figs. 1 and 2. The curves obtained from 330 to 435° are shown in Fig. 1 on a parabolic plot. The oxidations below 435° obeyed the parabolic law for at least 100 min. At 435° the curve was not parabolic beyond the first five minutes.

The results above 425° are shown in Fig. 2. The oxidations had an induction period followed by a rapid rise to an approximately linear shape after about 50 min. The induction period presumably corresponds to the formation of the first, adherent film. The linear portion is expected since the volume ratio is less than unity. However it is difficult to understand the sudden rise in the curves.

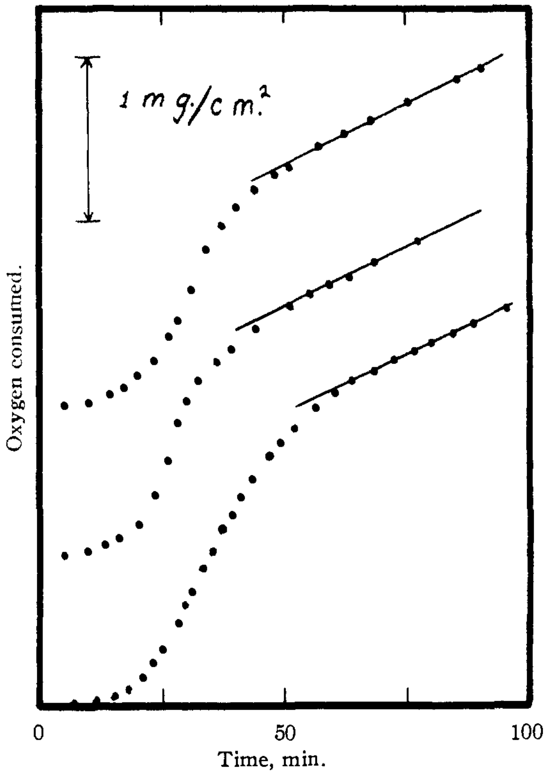

Fig. 2.—The oxidation of calcium at 425, 460 and 475°.

Acknowledgment.—The author is grateful to the Office of Naval Research for supporting this research.

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[3] D. Cubicciotti, THIS JOURNAL, to be published.

Cactus Alkaloids. II. Condensation of Mescaline with Formaldehyde by the Eschweiler–Clarke Reaction

BY JOSÉ A. CASTRILLÓN

In previous work in this Laboratory[1] a tetrahydroisoquinoline base was obtained in an attempt to synthesize trichocereine, *i.e.*, N-dimethylmescaline, by methylation of mescaline with formic acid–formaldehyde. This base has now been characterized as N-methyl-6,7,8-trimethoxy-1,2,3,4-tetrahydroisoquinoline. It is a new compound related to the *anhalonium* alkaloids, and can be expected to occur in nature, since it may be derived from anhalinine by an N-methylation or from anhalidine by an O-methylation.

Only one reference to cyclization during the Eschweiler–Clarke reaction with phenethylamines has been found in the literature,[2] though the cyclizing action of formaldehyde with the aid of a

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[1] L. Reti and J. A. Castrillón, THIS JOURNAL, **73**, 1767 (1951).

[2] J. S. Buck and R. Baltzly, *ibid.*, **64**, 2263 (1942), report that attempts to prepare 3,4-dimethoxyphenethylbenzylmethylamine from benzylhomoveratrylamine by this method, gave unsatisfactory results, probably owing to partial cyclization.

condensing agent such as hydrochloric acid is well known. In this particular case it can be explained by the presence of methoxyl groups in positions 3 and 5 which activate the 6-position in the ring. It must be remembered that phenethylamine,[3] hordenine[4] and 2,5-dimethoxyphenethylamine[5] give the dimethyl tertiary amines in good yields.

The usual technique has been followed[6] and after alkalinization and extraction with ether, a new base was obtained in a 51% yield. Under more drastic conditions the yield was increased to 80%.

The base was isolated as its hydrochloride which was not identical with that of trichocereine. Since the structure of this last compound is well established, this fact suggested that the reaction had led to a tetrahydroisoquinoline derivative.

A definite proof was provided by the oxidation of the hydrochloride which gave N-methyl-3,4,5-trimethoxyphthalimide, identical with a synthetic sample.[7]

Experimental

Pure mescaline (1.95 g.), 97.5% by weight formic acid (2.20 g.) and 40% "formalin" (1.53 ml.) were heated on the steam-bath for 12 hours. The reaction mixture was diluted with 70 ml. of water and strongly alkalinized with 20 ml. of 20% sodium hydroxide solution. After 4 extractions with ether the aqueous solution was exhausted of alkaloid. The collected extracts were dried over anhydrous sodium sulfate and the ether removed. An oily, slightly yellowish base (1.12 g.) was obtained (yield 51.2%).

It was taken up in 18 ml. of acetone, filtered and 0.45 ml. of concentrated hydrochloric acid added. On cooling to 0° and scratching, a colorless hydrochloride crystallized. It was collected, washed three times with 5 ml. of cold acetone and dried, weight 0.67 g. A second crop of less pure hydrochloride was obtained from the mother liquors. The first crop was recrystallized twice from absolute alcohol, m.p. 215–216° (cor.); mixed with trichocereine hydrochloride m.p. 180°.

Anal. Calcd. for $C_{13}H_{19}O_3N \cdot HCl$: C, 57.03; H, 7.36; OCH_3, 34.01; CH_3, 22.0. Found: C, 57.04; H, 7.49; OCH_3, 33.81; CH_3, 22.5.

Another experiment was carried out with a mixture of mescaline (0.86 g.), 93% in weight formic acid (1.81 g.) and 40% "formalin" (1 ml.) which was refluxed for eight hours in the oil-bath. Under these conditions 0.77 g. of the base was obtained (79.7%).

Methiodide.—The free base (0.19 g.), prepared from the hydrochloride, was dissolved in acetone (2 ml.) and methyl iodide added (0.1 ml.). A spontaneous exothermic reaction followed, and after 24 hours standing, the methiodide was filtered and washed 6 times with 1 ml. of acetone each time. Dry, it weighed 0.25 g., m.p. 210° (cor.). After three recrystallizations from alcohol a constant m.p. 215° (cor.), in agreement with that given by Späth,[8] (211.5–212.5°) who prepared this compound from anhalinine, was reached.

Anal. Calcd. for $C_{14}H_{22}O_3NI$: C, 44.34; H, 5.84; OCH_3, 24.54. Found: C, 44.87; H, 5.57; OCH_3, 25.18.

The **picrate** was precipitated from the hydrochloride (0.20 g.) and picric acid (0.17 g.) in alcohol. When recrystallized three times from the same solvent, it had m.p. 135–137° (cor.).

Anal. Calcd. for $C_{13}H_{19}O_3N \cdot C_6H_3O_7N_3$: N, 12.01. Found: N, 12.22.

Oxidation.—The hydrochloride (0.16 g.) was dissolved in water (50 ml.) and alkalinized with 2 ml. of 1 *N* sodium hydroxide. Permanganate solution (1.8%) was then added in small portions, finally with heating on the steam-bath. The total volume used up was 38 ml. The clear solution obtained after passing in sulfur dioxide was acidified with sulfuric acid and extracted thoroughly with chloroform. After evaporating the solvent, the residue (30 mg.) was taken up in hot water and filtered. This solution was concentrated to 1 ml. and the crystalline precipitate which separated was sublimed at 5 mm. pressure. A few milligrams of colorless needles melting at 125° (cor.) were collected. Mixed with an authentic sample of N-methyl-3,4,5-trimethoxyphthalimide, m.p. 127° (cor.), it melted at 126° (cor.).

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(3) R. N. Icke, B. B. Wisegarver and G. A. Alles, "Organic Syntheses," Vol. XXV, John Wiley and Sons, Inc., New York, N. Y., 1945, p. 89.

(4) Y. Raoul, *Compt. rend.*, **204**, 74 (1937).

(5) B. Baltzly and J. S. Buck, THIS JOURNAL, **62**, 161 (1940). Dr. R. Baltzly, in a private communication, kindly revealed to us the conditions used in their work, which were essentially those of Eschweiler (heating with formalin in a bomb). The Eschweiler–Clarke was tried by Baltzly and Buck on β-(2,5-dimethoxyphenyl)-propylamine and was found to give a product different from β-(2,5-dimethoxyphenyl)-propyl dimethylamine. It was also found that the Eschweiler–Clarke method gave tetrahydroisoquinolines in varying amounts and purity from homoveratrylamine.

(6) H. T. Clarke, H. B. Gillespie and S. Z. Weisshaus, *ibid.*, **55**, 4571 (1933).

(7) R. H. F. Manske and H. L. Holmes, *ibid.*, **67**, 95 (1945).

(8) E. Späth, *Monatsh*, **42**, 113 (1921).

Steroid Tetrahydropyranyl Ethers

BY WILLIAM G. DAUBEN AND H. LEON BRADLOW

In connection with other studies in this Laboratory[1] the synthesis and cleavage of tetrahydropyranyl ethers[2] of steroids have been investigated. This work was substantially completed before we learned of the similar work of Ott and co-workers.[3] It has been found that the tetrahydropyranyl ether of cholesterol can be prepared in good yield by employing an excess of dihydropyran as the solvent. Following the same procedure, the tetrahydropyranyl ether of methyl Δ^5-homocholenate was obtained in fair yield but the preparation of the ether of 3β-hydroxy-Δ^5-norcholesten-25-one gave erratic results. Good yields, in this latter case, could be obtained only when careful attention was paid to the addition of the acid catalyst (see Experimental). The yield was not improved in this instance by applying the procedure of Ott.[4]

Both dilute hydrochloric acid and catalytic amounts of *p*-toluenesulfonic acid in alcohol effected cleavage of the ether to the free sterol, though better yields were obtained when the sulfonic acid procedure was employed. It was found that when cholesteryl tetrahydropyranyl ether was refluxed with acetic acid or acetic anhydride as solvent for four hours, a mixture of cholesteryl acetate and the original ether was obtained. This mixture which had a constant melting point could not be separated by fractional crystallization. Treatment of the ether with boiling acetic acid or acetic anhydride for 24 hours or with acetic acid plus 1% hydrochloric acid gave the pure acetate in good yield.

In addition cyclohexyl tetrahydropyranyl ether was prepared in an orientating run.

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(1) W. G. Dauben and H. L. Bradlow, THIS JOURNAL, **72**, 4248 (1950).

(2) (a) G. F. Woods and D. N. Kramer, *ibid.*, **69**, 2246 (1947); (b) W. E. Parham and E. L. Anderson, *ibid.*, **70**, 4187 (1948).

(3) A. C. Ott, M. E. Murray, R. L. Pederson and M. H. Kuizenga, Abstract of the 117th Meeting of the American Chemical Society, Philadelphia, Penna., 1950, p. 9K.

(4) We are indebted to Dr. Ott for details of their method.

Experimental[5]

Cholesteryl Tetrahydropyranyl Ether.—A slurry of 5.00 g. (13 mmoles) of cholesterol and 20 ml. of dihydropyran was treated with two drops of concentrated hydrochloric acid and shaken vigorously for five minutes. At the end of this time all of the steroid had dissolved. After standing 12 hours at room temperature, the semi-solid mass was diluted with ether and processed as previously described.[2b] The solid residue was recrystallized from ethanol to give 5.01 g. (82%) of the ether, m.p. 151.5–152.5°. Recrystallization raised the melting point to 154.5–155.5°, $[\alpha]^{23}\text{D}$ −35.9° in chloroform.

Anal. Calcd. for $C_{32}H_{54}O_2$: C, 81.62; H, 11.56. Found: C, 81.80; H, 11.56.

3β-Hydroxy-Δ⁵-homocholenic Acid.—A solution of 1.00 g. (2.40 mmoles) of 3β-acetoxy-Δ⁵-cholenic acid in 10 ml. of dry benzene and 4 ml. of oxalyl chloride was heated at 50° for two hours. The solution was then concentrated to dryness at 50° *in vacuo*. Two 10-ml. portions of dry benzene were added and distilled under reduced pressure to remove the last traces of oxalyl chloride. The acid chloride, in 10 ml. of dry benzene, was added dropwise to a stirred solution of diazomethane (prepared from 1.1 g. of nitrosomethylurea) in 60 ml. of methylene chloride. After standing 12 hours, the solution was filtered, concentrated at reduced pressure and the residue treated with 100 ml. of methanol and freshly precipitated silver oxide (prepared from 10 ml. of 10% silver nitrate solution). The solution was slowly brought to reflux temperature, refluxed for one hour, treated with Norit, filtered and concentrated. The residue was refluxed with 5.00 g. of potassium hydroxide in 50 ml. of methanol and 40 ml. of water under a nitrogen atmosphere. The solution was filtered and acidified with concentrated hydrochloric acid. The suspension after standing for 12 hours, was centrifuged and dried overnight at 60°. The crude product weighed 0.72 g. (72%). After two recrystallizations from methanol–water, the acid melts from 197.6–199.2°. Hattori[6] reported a m.p. of 210–215°.

Anal. Calcd. for $C_{25}H_{40}O_3$: C, 77.23; H, 10.38. Found: C, 77.52; H, 10.53.

For conversion to the methyl ester the crude acid may be used.

Methyl 3β-Hydroxy-Δ⁵-homocholenate.—An ethereal solution of the crude acid was added slowly to an excess of diazomethane in ether at 0°. The solution was allowed to come to room temperature and the excess diazomethane removed with a slight excess of formic acid. The ethereal solution was washed with dilute sodium bicarbonate solution and water, dried and concentrated. The crude ester was chromatographed on alumina. After developing with benzene, the ester was eluted with 1% methanol in benzene. Recystallization from methanol gave 80% of white plates, m.p. 85.6–87.0°.

Anal. Calcd. for $C_{26}H_{42}O_3$: C, 77.32; H, 10.52. Found: C, 77.04; H, 10.24.

Methyl 3β-Hydroxy-Δ⁵-homocholenate Tetrahydropyranyl Ether.—Concentrated hydrochloric acid (two drops) was added to a solution of 0.63 g. of the methyl homocholenate in 10 ml. of dihydropyran with vigorous shaking. The reaction solution was allowed to stand for 24 hours and then processed in the usual fashion.[2b] The crude material was recrystallized from ethanol–water, yield 0.20 g. (30%), m.p. 92.5–93.0°, $[\alpha]^{25}\text{D}$ −36.6° in chloroform.

Anal. Calcd. for $C_{31}H_{48}O_4$: C, 76.81; H, 9.98. Found: C, 76.93; H, 10.40.

3β-Hydroxy-Δ⁵-norcholesten-25-one Tetrahydropyranyl Ether.—A solution of 1.00 g. (2.6 mmoles) of norolone in 20 ml. of dihydropyran was prepared by gentle warming and then carefully cooled to room temperature. Concentrated hydrochloric acid (0.4 ml.) was added dropwise to this solution over a period of four minutes with vigorous agitation. After the addition of each drop of acid, the solution was shaken until the blackish precipitate, which formed, redissolved. The solution was allowed to stand for 48 hours and then processed in the usual fashion.[2b] The first recrystallization gave a sirupy mixture which was best separated by centrifugation. After two more recrystallizations from alcohol–water, the product melted at 104.9–106.2°. The yield was 0.71 g. (57%), $[\alpha]^{28}\text{D}$ −28.6° in chloroform.

Anal. Calcd. for $C_{31}H_{50}O_3$: C, 79.11; H, 10.69. Found: C, 79.45; H, 10.85.

Hydrolysis of Cholesteryl Tetrahydropyranyl Ether.—A solution of 1.00 g. (2.12 mmoles) of cholesteryl tetrahydropyranyl ether and 0.05 g. of *p*-toluenesulfonic acid in 15 ml. of ethanol was refluxed for one hour, concentrated to half volume, diluted with water and cooled. Filtration gave 0.80 g. (97%) of lustrous plates, m.p. 146.0–147.5°. Concentrated hydrochloric acid may also be used as catalyst, though the yield is somewhat lower.

Acetolysis of the Ether to Cholesteryl Acetate.—A solution of 4.00 g. (8.15 mmoles) of the pyranyl ether in 25 ml. of acetic acid was refluxed for 24 hours, concentrated under reduced pressure and the residue dissolved in ether. The ethereal solution was washed with dilute sodium carbonate solution and saturated sodium chloride solution, dried and concentrated. The solid acetate was recrystallized twice from methanol to give 2.57 g. (70.5%) of cholesteryl acetate, m.p. 113.1–113.8°, undepressed upon admixture with an authentic sample. Acetic anhydride as solvent gave almost identical results. When the reaction time was cut to three or four hours, a mixture of unchanged ether and cholesteryl acetate was obtained, which melted at 95.5–97.0° after sintering at 92° (unchanged by repeated recrystallization), $[\alpha]^{23}\text{D}$ −40.9° in chloroform. The optical rotation was intermediate between that of the ether, −35.9°, and that of the acetate, −47.5°. An equimolar mixture of the ether and the acetate, thrice recrystallized from methanol, melted at 95.0–97.1°, $[\alpha]^{21}\text{D}$ −38.0° in chloroform.

Cyclohexyl Tetrahydropyranyl Ether.—Three drops of concentrated hydrochloric acid were added dropwise to a solution of 20.0 g. (0.2 mole) of cyclohexanol in 35 ml. of dihydropyran and the reaction allowed to stand overnight. The solution was then diluted with ether and worked up as usual. After 2.07 g. of forerun, 30.68 g. (82.5%) of the ether was obtained, b.p. 94–95° (5 mm.), $n^{25}\text{D}$ 1.4642.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.68; H, 10.95. Found: C, 71.83; H, 10.80.

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[5] All melting points are corrected. All boiling points are uncorrected. All analyses are by the Microanalytical Laboratory of the Dept. of Chemistry, Univ. of California

[6] J. Hattori, *J. Pharm. Soc. Japan*, **58**, 548 (1938).

Reaction of Wijs Iodine Number Reagent with the *exo*-Isomer of Endomethylenetetrahydrophthalic Anhydride

BY C. H. HELBING

In connection with research on cyclopentadiene, *endo*-3,6-endomethylenetetrahydrophthalic anhydride was converted to the *exo*-isomer by a process which in its essential details followed that reported by Alder and Stein, *et al.*[1] The *endo*-isomer was prepared from cyclopentadiene and maleic anhydride in methyl ethyl ketone at 20–40°.

The iodine number determined by the Wijs method,[2] which utilizes iodine monochloride, on the *exo*-isomer was substantially the theoretical value as calculated for 3,6-endomethylenetetrahydrophthalic anhydride (154.7). The iodine number determined in the same manner on the *endo*-isomer was substantially zero. A determination on a known mixture gave about the expected result with the assumption that the *exo*-form reacts with iodine monochloride and the *endo*-form does not. This information should be useful in determining the isomers present in cyclopentadiene adducts.

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[1] K. Alder, G. Stein, Wolfgang Eckardt, Rudolf Freiherr v. Buddenbrock and Stephan Schneider, *Ann.*, **504**, 216 (1933); *C. A.*, **27**, 5311 (1933).

[2] ASTM: D 555-41-9.

Experimental details are given in Table I.

TABLE I

Isomer	M.p., °C.	Iodine number Found	Iodine number Calcd.
endo	151–162[a]	3.4	154.7
exo	142–145	151.9	154.7
Mixture			
69% *endo*	118–133	49.6	49.4
31% *exo*			

[a] This melting point was taken on *endo*-3,6-endomethyleneteterahydrophthalic anhydride which was fused and allowed to resolidify. The crystals of the *endo*-isomer which separated from methyl ethyl ketone as reaction product of maleic anhydride and cyclopentadiene melted at 164° before fusion.

We wish to thank Mr. E. F. Berger for iodine number determinations.

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Preparation of Organopolysilanes

BY HENRY GILMAN, TSE CHENG WU, HOWARD A. HARTZFELD, GERALD A. GUTER, ARTHUR G. SMITH, JACK J. GOODMAN AND SCOTT H. EIDT

The silicon–silicon bond is in general much less stable than the carbon–carbon bond (Si–Si, 45 kcal./mole; C–C, 80 kcal./mole[1]). While the length of the carbon–carbon chain is almost unlimited, the silicon–silicon chains known at the present time are relatively short. In the polysilane series the longest silane ever reported[2] is Si_6H_{14}. Silicon chlorides from $SiCl_4$ to Si_6Cl_{14} are well known.[3] Schwarz and co-workers[4,5] reported the preparation of $Si_{10}Cl_{22}$ and $Si_{25}Cl_{52}$ by heating $SiCl_4$ in a hydrogen and in a nitrogen atmosphere, respectively.

The organosubstituted silicon chains which have been made are rather small. Although there are a few known hexasubstituted disilanes, no octasubstituted trisilane has been reported. Schumb and Saffer[6] treated octachlorotrisilane with phenylmagnesium bromide, and they obtained a mixture of tetraphenylsilane and hexaphenyldisilane instead of octaphenyltrisilane. The aryl organosilicon chains of greater length which have been reported were prepared by the action of sodium on diphenyldichlorosilane and closely related compounds. By this method Kipping and co-workers[7a] were able to isolate two compounds with the formula $(C_6H_5)_8Si_4$ and two other substances with the formulas $[(C_6H_5)_2Si]_n$, with n having a value of 6 or 8. Recently, Burkhard,[7b] using a similar procedure, showed in an interesting study that polydimethylsilanes can be prepared from dimethyldichlorosilane and sodium.

We are now reporting a new approach for the syntheses of organopolysilanes. When two moles of triphenylsilylpotassium is treated with one mole of diphenyldichlorosilane in ether, octaphenyltrisilane is formed. When one mole of triphenylsilylpotassium is treated with one mole of diphenyldichlorosilane, pentaphenylchlorodisilane can be isolated. Pentaphenylchlorodisilane is an interesting compound because compounds of this type may be coupled to form organopolysilanes by doubling the length of the silicon chain.

$$(C_6H_5)_3SiSi(C_6H_5)_3 \xrightarrow{\text{Na-K}} 2(C_6H_5)_3SiK$$

$$2(C_6H_5)_3SiK + (C_6H_5)_2SiCl_2 \longrightarrow (C_6H_5)_8Si_3 + 2KCl$$

$$(C_6H_5)_3SiK + (C_6H_5)_2SiCl_2 \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_2Cl + KCl$$

Experimental

Triphenylsilylpotassium.—In a previous paper from this Laboratory[8] there was described the preparation of triphenylsilylpotassium from hexaphenyldisilane and sodium–potassium alloy. (Due precautions should be exercised in the preparation and handling of this alloy.) Since then we found that the amount of ether used as a solvent affected the initiation of the reaction. In general an increase in the amount of solvent used increased the time for the appearance of the color of the organosilicon–metallic compound. After some studies the following procedure worked satisfactorily, and it has been checked more than twenty times.

In a dry three-necked flask fitted with a Trubore glass blade stirrer, a gas inlet tube, and a glass stopper were placed 4 g. (0.0077 mole) of hexaphenyldisilane,[9] 1 ml. of sodium–potassium alloy (1:5) and 10 ml. of anhydrous ether, after the flask had been swept with dry, oxygen-free nitrogen. The slurry was stirred vigorously at room temperature. Usually, after 5 to 10 minutes a greenish-yellow color began to form, indicating the start of the reaction. About 30 minutes later a distinct tan mixture was formed. Then 50 ml. of anhydrous ether was added to the reaction mixture against a stream of nitrogen.[10] The mixture was stirred at room temperature for about 20 hours. At the end of this period a suspension with a color ranging from dark greenish-brown to tan was formed. Mercury was added (caution!) dropwise to the reaction mixture until a liquid amalgam was formed. The amalgam was then stirred with the reaction mixture for one and one-half hours in order to dissolve all the excess sodium–potassium alloy. The triphenylsilylpotassium suspension was separated from the liquid amalgam by forcing it through a glass tubing by the pressure of nitrogen into a dry nitrogen-filled dropping funnel. Color Test I[11] for the clear supernatant liquid was negative, whereas the precipitate gave an intense bluish-violet color in both organic and aqueous layers of the Color Test.

Octaphenyltrisilane.—A triphenylsilylpotassium suspension prepared according to the procedure described in the last paragraph was added fairly rapidly to 1.5 g. (0.0059 mole) of diphenyldichlorosilane dissolved in 20 ml. of anhydrous ether (in a nitrogen atmosphere). Some heat was evolved, and there was very little color change. The reaction mixture was stirred for 9 hours at room temperature. Color Test I[11] at this stage was positive (bluish-green), probably due to the slight excess of triphenylsilylpotassium present. The reaction mixture was filtered by suction. The gray residue was boiled 30 minutes with 50 ml. of dry benzene and filtered hot. On standing, a small amount of white precipitate was formed. This was removed by filtration. The solids melted at about 270° to form a turbid

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(1) K. S. Pitzer, THIS JOURNAL, **70**, 2140 (1948).

(2) A. Stock and C. Somieski, *Ber.*, **49**, 111 (1916).

(3) See, for example, J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VI, Longmans, Green and Co., New York, N. Y., 1940, p. 960 ff.

(4) R. Schwarz and H. Meckbach, *Z. anorg. u. allgem. Chem.*, **232**, 241 (1937).

(5) R. Schwarz and C. Danders, *Chem. Ber.*, **80**, 444 (1947).

(6) W. C. Schumb and C. M. Saffer, Jr., THIS JOURNAL, **61**, 363 (1939).

(7a) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 830, 848 (1921); F. S. Kipping, *ibid.*, **123**, 2590, 2598 (1923); *ibid.*, **125**, 2291 (1924).

(7b) C. A. Burkhard, THIS JOURNAL, **71**, 963 (1949).

(8) H. Gilman and T. C. Wu, THIS JOURNAL, **73**, 4031 (1951).

(9) Hexaphenyldisilane was prepared according to the method described by H. Gilman and G. E. Dunn, *ibid.*, **73**, 5077 (1951). It appears desirable to extend the reflux period to about 12 hours.

(10) It was observed that if the remainder of the ether was added before about 30 minutes, the yellow color which had formed faded away. It took some time for the reappearance of the color.

(11) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

melt which became clear liquid at about 320°. It was believed to be impure hexaphenyldisilane. The benzene extract was concentrated to about 10 ml., and to this was added 20 ml. of petroleum ether (b.p. 60–70°). On cooling to room temperature 2.2 g. (53% based on diphenyldichlorosilane) of white solids melting at 238–244° was obtained by filtration. The crude product was recrystallized three times from a mixture of benzene and ethanol to give 1.2 g. (29%) of colorless needles melting at 260–262° to form a somewhat gelatinous mass which became water-clear liquid at 266° (uncor.).

Anal. Calcd. for $C_{48}H_{40}Si_3$: Si, 12.00. Found: Si, 11.98, 11.84.

Three check runs were made. In two of these runs a product melting at 302–303° was isolated. Analysis showed that it, too, had the composition of octaphenyltrisilane. From molecular model studies we suspected that this inconsistency in the melting points of these two products might possibly be due to the existence of isomeric forms. Further studies are now in progress.

Pentaphenylchlorodisilane.—A triphenylsilylpotassium suspension prepared according to the procedure described above was added fairly rapidly to 4 g. (0.016 mole) of diphenyldichlorosilane dissolved in 20 ml. of ether. It was noticed that the first few drops of triphenylsilylpotassium was decolorized immediately when it was added to the diphenyldichlorosilane solution. When addition was completed, a gray suspension was formed. Color Test I[11] immediately after the addition was negative. The mixture was stirred 1 hour at room temperature and was filtered by suction. The solvent was distilled from the filtrate to give 7.1 g. of colorless solids melting at 120–140°. The crude product was recrystallized twice from petroleum ether (b.p. 60–70°) to give colorless granular crystals melting at 154–155° (uncor.). The yield of pure product was 3.7 g. (50%).

Anal. Calcd. for $C_{30}H_{25}Si_2Cl$: Si, 11.79; Cl, 7.43. Found: Si, 11.76, 11.81; Cl, 7.42, 7.36.

Pentaphenylchlorodisilane is an interesting compound because even though it can be hydrolyzed in aqueous basic solution to give the corresponding hydroxy compound, still, unlike the triphenylchlorosilane, it is quite stable in air. A sample of this compound was put in a vial loosely plugged with cotton. After 3 months there was no depression in its melting point. Its preparation has been checked several times.

From some preliminary work it was found that pentaphenylchlorodisilane can be treated with sodium in boiling xylene to give a white solid, presumably decaphenyltetrasilane. Further work is now in progress.

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AMES, IOWA

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Phenylphosphine[1]

BY ROBERT J. HORVAT AND ARTHUR FURST

Phenylphosphine has been previously prepared by reducing dichlorophenylphosphine directly with anhydrous hydrogen iodide,[2,3] or by first converting the dichlorophenylphosphine to diiodophenylphosphine hydrogen iodide and treating this with absolute alcohol.[4] Yields were increased only after many hours of reaction.

It is possible to obtain phenylphosphine in much shorter time and in comparable over-all yields by simply reducing the dichlorophenylphosphine with lithium aluminum hydride.

Experimental

To an ice-cold solution of 4.18 g. (0.11 mole) of lithium aluminum hydride in 200 ml. of absolute ether was added drop by drop 35.5 g. (0.2 mole) of dichlorophenylphosphine (Victor Chemical Works) dissolved in 200 ml. of absolute ether. The reaction mixture turned yellow and soon began to reflux. After the addition was complete the mixture was refluxed for one hour, cooled and filtered through glass wool. In an atmosphere of nitrogen the ether was first removed; then the phenylphosphine was distilled and collected as a colorless liquid at 160–161°. The yield was 5.6 g. (25.4%); hydrogen iodide salt, m.p. 136° (uncor.).

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[1] A grant-in-aid from Research Corporation is gratefully acknowledged; also the technical assistance of O. Clark Chisim.

[2] A. Michaelis, *Ber.*, **7**, 6 (1874).

[3] H. Lecoq, *Bull. soc. chim. Belg.*, **42**, 199 (1933).

[4] H. Kohler and A. Michaelis, *Ber.*, **10**, 807 (1877).

The Solubility of Aniline Hydrochloride in Water

BY EDWARD H. HOUSE AND JOHN H. WOLFENDEN

Three values for the solubility of aniline hydrochloride are recorded in the literature and regularly quoted in works of reference. Two of these relate to 25° and are in fair agreement; at this temperature C. J. Peddle and W. E. S. Turner[1] report that 100 g. of water dissolves 107.1 g. of the salt while N. V. Sidgwick, P. Pickford and B. H. Wilsdon[2] report that 100 g. of the saturated solution contains 52.1 g. of the salt. The third solubility determination relates to 15°, at which temperature S. v. Niementowski and J. v. Roszkowski[3] report that 100 cc. of water dissolves 17.762 g. of aniline hydrochloride. This last figure is at variance with common observation in the purification of the salt by recrystallization, and suggests a remarkably high temperature coefficient of solubility. The molal heat of solution computed from the recorded solubilities at 15° and 25° implies an absorption of about 29 kcal. of heat, a value much larger than the value of 2.7 kcal. measured by Louguinine,[4] than the heats of solution of other amine hydrochlorides, which commonly range between 1 and 4 kcal. per mole, and than the heat of fusion of the salt as deduced from the cryoscopic data of Leopold[5] (*ca.* 2 kcal. per mole).

The paucity of information about the solubility of this common organic compound and the implausibility of the only determination at any temperature other than 25° prompted us to measure the solubility over the temperature range from 0° to 100°. Saturated solutions of the pure recrystallized salt in water containing 0.2% of aniline to repress hydrolysis were analyzed by titration with

TABLE I

SOLUBILITY OF ANILINE HYDROCHLORIDE

Temp., °C.	g./100 g. H_2O	Mole fraction
0	63.50	0.08112
15	88.36	.1094
25	107.35	.1299
40	143.7	.1665
100	396	.355

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[1] C. J. Peddle and W. E. S. Turner, *J. Chem. Soc.*, **103**, 1202 (1913).

[2] N. V. Sidgwick, P. Pickford and B. H. Wilsdon, *ibid.*, **99**, 1122 (1911).

[3] S. v. Niementowski and J. v. Roszkowski, *Z. physik. Chem.*, **22**, 145 (1897).

[4] Cited by M. Berthelot, *Ann. chim. Phys.*, 6e. ser., **21**, 355 (1890).

[5] G. H. Leopold, *Z. physik. Chem.*, **71**, 59 (1910).

standard alkali using brom thymol blue as indicator. Measurements were carried out at 0°, 15°, 25°, 40° and, with reduced accuracy, at 100°. At least six determinations were carried out at each temperature. The best value for the solubility at each temperature is summarized in Table I.

The logarithm of the mole fraction N plotted against the reciprocal of the absolute temperature T gives a close approximation to a straight line. The equation

$$\log N = 1.344 - \frac{665}{T}$$

corresponding to a heat of solution of 3.04 kcal. per mole, may be relied upon to give the solubility of aniline hydrochloride in water to within 0.7% over the temperature range 0° to 50° and to within 2.5% over the range 50° to 100°. It will be noted that the previously accepted solubility at 15° is almost exactly one-fifth of the emended value.

DEPARTMENT OF CHEMISTRY
DARTMOUTH COLLEGE
HANOVER, NEW HAMPSHIRE
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The Spectrophotometric Determination of the Rate Constant of First Order Reactions[1]

BY EDWARD L. KING

The optical density of a solution in which the change A → B is occurring is given by the equation

$$D_t = \log I_0/I = l\,\{\epsilon_A(A)_t + \epsilon_B(B)_t\}$$

where l is the cell length in cm., ϵ_A and ϵ_B are the molar extinction coefficients of A and B and $(A)_t$ and $(B)_t$ are the molar concentrations at time t. If the rate law for this change is $d(A)/dt = -k(A)$, the dependence of D upon t is given by equation 1

$$\{D_t/l(A)_0 - \epsilon_B\} = (\epsilon_A - \epsilon_B)\,e^{-kt} \quad (1)$$

and thus a plot of the logarithm of the quantity on the left side of the equation *versus* time will give a straight line of slope $-k$. To make such a plot, however, requires knowledge of the quantities $(A)_0$ and ϵ_B. In a modification of the method suggested by Guggenheim,[2] the rate constant may be obtained without knowledge of either of these two quantities.

Equation 2 relates the optical densities of the solution at times t and $t + \tau$

$$(D_t - D_{t+\tau}) = l(A)_0\,(1 - e^{-k\tau})(\epsilon_A - \epsilon_B)\,e^{-kt} \quad (2)$$

and it is seen that a plot of logarithm $(D_t - D_{t+\tau})$ *versus* time would give a straight line of slope $-k$ if τ is a constant time interval. In the usual procedure readings of the optical density of the reaction mixture *versus* a solvent "blank" would be made at times: $t_1, t_2, \cdots, t_n, t_1 + \tau, t_2 + \tau, \cdots$ and $t_n + \tau$. In view of the relationship

$$D' = (D_t - D_{t+\tau}) = \left\{\log\frac{I_0}{I_t} - \log\frac{I_0}{I_{t+\tau}}\right\} = \log\left(\frac{I_{t+\tau}}{I_t}\right)$$

a convenient means of determining the first order rate constant is available. If in the two cells in the usual arrangement for spectrophotometric measurements, there are placed two identical reaction mixtures in one of which the reaction has been proceeding for a time τ longer than in the other, the value of the "optical density," D', of the less transparent sample compared with the more transparent sample is the value of the desired $(D_t - D_{t+\tau})$. A plot of logarithm D' *vs.* t will be a straight line of slope $-k$. As was true in the conventional Guggenheim method, the time interval τ should be several times as great as the half-time of the reaction in order to obtain optimum precision.

The above considerations indicate a method for determination of the rate constant of a first order reaction in which the extinction of a reacting system is measured against that of an identical mixture at a different stage of the same reaction. This method has advantages compared to the conventional Guggenheim method applied to a spectral study in which a solvent "blank" is used in that fewer readings must be taken for the same number of points, the readings extend over a shorter time interval, and the readings need not be taken at planned time intervals. The somewhat larger slit widths which are required because of the absorption of the "blank" are a disadvantage in the study of reactions in which the rate of change of ϵ values for reactant and/or product with changing wave length is large.

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[1] This work was supported by a grant from the U. S. Atomic Energy Commission.

[2] E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

Sodium Perborate as a Reagent in Organic Chemistry. I. Preparation of Azo-Compounds

BY S. M. MEHTA AND M. V. VAKILWALA

Sodium perborate has received little or no attention as a reagent for organic oxidations. Serantes[1] found it to be satisfactory for the oxidation of benzoic acid. Allen and Clark[2] used it as a satisfactory substitute for sodium peroxide in many oxidation reactions and described its action on α-diketones. A study of sodium perborate as a reagent for the oxidation of organic compounds is underway in this Laboratory. The present paper describes the oxidation of aniline and a number of its para-substitution products with sodium perborate in acetic acid as a solvent.

In glacial acetic acid the corresponding azo-compound may be obtained in relatively pure form and, with the exception of aniline and *p*-anisidine, relatively free of tarry by-products. The yield of azo-compound varies with the temperature of reaction and with the concentration of the acetic acid. Maximum yields are obtained in glacial acetic acid and at temperatures of reaction between 40 to 50° (Table I). Addition of water to the acetic acid solvent markedly lowers the yield of oxidation product.

The product of the action of sodium perborate on aniline cannot be recovered by direct crystallization but must be removed from the reaction mix-

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[1] M. T. Serantes, *Rev. farm.*, **65**, No. 4 (1923); *Anales asoc. quim. argentina*, **12**, 58 (1923); *C. A.*, **19**, 1134 (1925).

[2] C. F. H. Allen and J. H. Clark, *J. Chem. Education*, **19**, 72 (1942).

TABLE I

OXIDATION OF AROMATIC AMINES[a] WITH SODIUM PERBORATE[b]

Amine	Reaction temp., °C.[c]	Normality of acetic acid	Product	M.p., °C. found	M.p., °C. reported	Yield, %
p-Bromoaniline	35	20.68[d]	4,4'-Dibromoazobenzene	204–205	205[e]	44.08
	40	20.68	4,4'-Dibromoazobenzene			49.40
	40	18.93	4,4'-Dibromoazobenzene			20.83
	40	10.67	4,4'-Dibromoazobenzene			7.30
	45	20.68	4,4'-Dibromoazobenzene			50.42
p-Chloroaniline	35	20.68	4,4'-Dichloroazobenzene	187	188[f]	37.67
	40	20.68				43.61
	40	18.93				19.11
	40	10.67				6.52
	45	20.68				44.77
	50	20.68				48.37
p-Toluidine	35	20.68	4,4'-Azotoluene	144	144[g]	15.17
	40	20.68				20.08
	45	20.68				26.43
	50	20.68				29.95
p-Nitraniline	40	20.68	4,4'-Dinitroazobenzene	216	216[h]	20.31
p-Aminobenzoic acid	40	20.68	Azobenzene-4,4'-dicarboxylic acid	Dec. at 330	Dec. at 330[i]	38.8

[a] One-hundredth mole dissolved in 20 cc. of acetic acid. [b] Sufficient to yield 0.01 atom proportion of oxygen (1.66 g.). [c] The reaction was carried out for 3 hours. [d] Glacial acetic acid. [e] Heilbron and Bunbury, "Dictionary of Organic Compounds," Vol. 1, Eyre and Spottiswoode Ltd., 1943, p. 680. [f] *Ibid.*, p. 739. [g] *Ibid.*, p. 892. [h] Zincke und Kuchinbecker, *Ann.*, **330**, 28 (1904). [i] Heilbron and Bunbury, ref. *e*, p. 202.

ture by steam distillation. Anisidine undergoes too rapid oxidation in glacial acetic acid yielding an intractable black amorphous powder. However, the sodium perborate oxidation of anisidine can be successfully accomplished in aqueous media.

In general the sodium perborate–acetic acid reagent produces higher yields of azo-compounds by oxidation of aniline and its para-substitution products than equivalent mixtures of hydrogen peroxide–acetic acid. Addition of an amount of boric acid, equivalent to that in sodium perborate, to this latter mixture improves the yields of oxidation products.

Experimental[3]

General Procedure.—The aromatic amine and sodium perborate are individually dissolved in a convenient volume of glacial acetic acid and after adding the solution of the aromatic amine to that of perborate, allowed to react at about 40 to 50°. After cooling to room temperature, the crystals so obtained are collected and washed with water to remove the adhering acetic acid. No other process for the isolation or purification of the crystals is required except in the case of aniline and anisidine. Table I summarizes the data obtained for a series of para-substituted aromatic amines in which variations in reaction temperature and normality of acetic acid were studied.

Oxidation of Aniline.—Freshly distilled aniline (3.72 g., 0.04 mole) was dissolved in 80 cc. of glacial acetic acid and added to the same volume of glacial acetic acid containing 6.628 g. (0.04 atom of oxygen). After 3 hours reaction at 40°, the mixture was steam distilled. The solid distillate obtained (yield 17.9%) was recrystallized from absolute ethanol. The orange colored crystals weighed 0.547 g. (15.05%) and melted at 68°. The reported m.p. of azobenzene is 68°.[4]

Oxidation of Anisidine.—Sodium perborate (3.314 g., 0.02 atom of oxygen) dissolved in 75 cc. of distilled water was added to 2.46 g. (0.02 mole) of anisidine suspended in 75 cc. of water containing sodium acetate (8 g.) and the mixture allowed to stand at room temperature (29°) for 48 hours. The brown precipitate thus obtained was recovered by filtration, eluted with 40 cc. of absolute ethanol at room temperature (29°) yielding a yellow residue which after recrystallization from hot absolute ethanol yielded 0.3466 g. (13.43%) of bright yellow needles, m.p. 118° (turbid melt becoming clear at 133°). The reported m.p. of 4,4'-azoxy-anisole[5] is 118–119° clearing at 135°.

Hydrogen Peroxide, Boric Acid, Acetic Acid as Oxidation Media.—Experiments were carried out in order to compare the effect of (a) sodium perborate and acetic acid, (b) hydrogen peroxide, boric acid and acetic acid and (c) hydrogen peroxide and acetic acid. The sodium perborate used was 1.657 g. (0.01 atom of oxygen) dissolved in 40 cc. of glacial acetic acid. The hydrogen peroxide comprised 11.4 cc. of 1.75 *N* (0.01 atom of oxygen) dissolved in 40 cc. of glacial acetic acid. The quantity of boric acid (0.686 g.) was the same as present in 1.657 g. of sodium perborate. The reactions were carried out at 50° for three hours and the products recovered by the method described in the General Procedure.

YIELDS OF RECRYSTALLIZED PRODUCTS

	a	*b*	*c*
4,4'-Dibromoazobenzene	25.22	21.85	18.68
4,4'-Dichloroazobenzene	23.80	19.23	17.26
4,4'-Azotoluene	11.63	9.01	5.77

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[3] All melting points are uncorrected.

[4] Heilbron and Bunbury, "Dictionary of Organic Compounds," Vol. I, Eyre and Spottiswoode Ltd., 1943, p. 201.

[5] Heilbron and Bunbury, *ibid.*, p. 819.

New Esters of Pentaerythritol[1]

BY G. E. MCCASLAND AND DONALD ARTHUR SMITH[2]

For use in stereochemical studies, which we hope to describe in a later publication, the following compounds were prepared and characterized.

Experimental

Pentaerythritol Tetrachloroacetate (A).—Under anhydrous conditions 2.0 g. of pentaerythritol was refluxed with 8.3 g. of chloroacetyl chloride for 45 minutes. Excess acid chloride was then removed by vacuum distillation. The residue solidified on cooling, giving 7.0 g. of product, m.p.[3]

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[1] We are indebted to the National Research Council (Canada) for a grant in support of this work.

[2] Fellow of the Canadian Industries, Limited, 1949–1951.

[3] Melting and boiling points corrected. M.p.'s were determined on the Köfler micro-block. Analyses by Mr. R. Pyke.

65–87°. After two recrystallizations from ethanol, 5.4 g. (83%) of colorless leaflets, m.p. 94.5–96°, was obtained. Admixture of product from procedure (B) did not depress the m.p.

(B).—Under anhydrous conditions a mixture of 13.6 g. of pentaerythritol, 85.5 g. of chloroacetic anhydride and 0.5 g. of fused zinc chloride was boiled at 20 mm. pressure under reflux until the initial vigorous reaction had subsided, and then heated below the boiling point on a steam-bath for three hours. The (hot) mixture was poured into 200 ml. of water and allowed to stand overnight. The product separated as an oil. Addition to the mixture of 100 ml. of ethanol failed to cause crystallization. The aqueous ethanolic phase was separated and discarded. On addition of 50 ml. more ethanol to the non-aqueous phase, crystallization occurred. By filtration and washing with ethanol, 14.5 g. of colorless crystals, m.p. 55–56°, was obtained.

Recrystallization of 11.6 g. from 200 ml. of absolute ethanol gave 7.0 g. (16%) of colorless leaflets, m.p. 100.5–101°.

Anal. Calcd. for $C_{13}H_{16}Cl_4O_8$: C, 35.32; H, 3.65. Found: C, 35.42; H, 3.47.

By procedure (A) one obtains the product in much higher yield, and its purity is satisfactory for most purposes.

The compound gave a positive Beilstein halogen test, but reacted with alcoholic silver nitrate only after many minutes of boiling.

Reaction of *α-p*-Nitrophenylbutyryl Chloride with Pentaerythritol.—Finely divided, dry portions of *d,l-α-p*-nitrophenylbutyric acid (m.p. 118–120°)[4,5] (5.0 g.) and of phosphorus pentachloride (5.1 g.) were mixed. The mixture soon liquefied, with evolution of hydrogen chloride. The mixture was gently boiled for ten minutes, then phosphorus oxychloride was removed by vacuum distillation. The residue upon vacuum distillation gave 4.67 g. (86%) of *d,l-α-p*-nitrophenylbutyryl chloride as a bright yellow liquid of b.p. 172–174° (10 mm.), n^{26}D 1.5505, which could not be induced to crystallize. To characterize the product, it was treated with ethanol and sodium hydroxide under Schotten–Baumann conditions, giving *d,l*-ethyl *α-p*-nitrophenylbutyrate, b.p. 145–150° (2–3 mm.), n^{24}D 1.5202, d^{28} 1.133. The constants are in good agreement with those for the ester prepared[5] directly from the acid.

When the acid chloride (5.7 g.) was heated with 0.55 g. of pentaerythritol at 150° for 20 minutes, the product was obtained as a yellow oil, which solidified on prolonged shaking with ethanol to give 3.3 g. of material, m.p. 90–122°. After seven recrystallizations from ethanol the colorless product (0.66 g., 30%) still melted over a wide range (130–153°). The molecular weight (Rast method) was found to be 810 (theor. for $C_{43}H_{48}N_4O_{16}$, 901). It is presumably a mixture of the three theoretically possible racemic forms, and has not been further characterized.

***d,l*-Pentaerythritol Tetra-[2-(carbo-2-methylbutoxy)-6-nitrobenzoate].**—Under anhydrous conditions, 5.0 g. of *dextro*-2-methylbutyl 2-carboxy-6-nitrobenzoate[6] (m.p. 160–161°, $[\alpha]^{25}$D +2.56° (acetone, *c*, 32)) was refluxed with 10 ml. of thionyl chloride for one hour. After removal of thionyl chloride by vacuum distillation, the residue was recrystallized from dry petroleum ether, giving colorless leaflets of m.p. 60–62°. After two more recrystallizations, 4.5 g. (84%) of *dextro*-2-methylbutyl 2-chloroformyl-6-nitrobenzoate, m.p. 61–62°, $[\alpha]^{25}$D +0.69° (ethyl acetate, *c*, 17.3), was obtained.

To one gram of the acid chloride in 2 ml. of dry pyridine was added 0.10 g. of pentaerythritol. The warm mixture was cooled, and after 17 hours at 25° was added at 0° to 10 ml. of 10% sulfuric acid. The aqueous phase was decanted and the semi-solid organic residue recrystallized twice from ethanol, giving 0.75 g. (86%) of fine colorless needles, m.p. 111–114°. A sample was recrystallized again for analysis, and dried at 80° (10 mm.); m.p. 113–115°.

Anal. Calcd. for $C_{57}H_{64}N_4O_{24}$: C, 57.57; H, 5.43; N, 4.71. Found: C, 57.18; H, 5.17; N, 5.12.

Recrystallization from benzene–ligroin changed the m.p. to 85–95°, but when this low-melting form was recrystallized from ethanol the m.p. was restored to 113–115°.

The product gave no optical rotation and was apparently racemic.[7] An identical product was obtained when the same reactions were carried out with the 3-nitrophthalate of *d,l*-2-methylbutanol. A mixed m.p. on the two final products showed no depression.

Three racemic forms are theoretically possible for the pentaerythritol ester but thus far only the product above has been isolated.

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[4] C. S. Marvel and T. Chu, This Journal, **55**, 2841 (1933).

[5] A. L. Wilds and W. R. Biggerstaff, *ibid.*, **67**, 789 (1945).

[6] A. McKenzie, *J. Chem. Soc.*, **79**, 1135 (1901).

[7] Since the observed rotation of the acid chloride from the *dextro*-3-nitrophthalate was only + 0.12°, the racemization may have occurred during chlorination.

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Chloromycetin.[1] Related Compounds. The β-*p*-Nitrophenylserines

By G. W. Moersch, M. C. Rebstock, A. C. Moore and D. P. Hylander

Chloromycetin has been shown to be D_G-(−)-*threo*-2-dichloroacetamido-1-*p*-nitrophenyl-1,3-propanediol.[2] In exploring related substances, several authors[3,4,5] have reported on β-*p*-nitrophenylserine and its N-dichloroacetyl derivative which differs from Chloromycetin in having a carboxyl in place of the primary carbinol group. β-*p*-Nitrophenylserine has been prepared by (1) nitration of the N-acetate of Erlenmeyer's β-phenylserine,[3] by (2) direct nitration of Erlenmeyer's β-phenylserine,[4] by (3) the condensation of *p*-nitrobenzaldehyde with ethyl glycinate over sodium,[6] and recently by (4) the condensation of *p*-nitrobenzaldehyde with ethyl glycinate in alcohol solution without a catalyst.[7]

On the basis of microbiological testing, Billet[8] has claimed from unpublished work, a difference suggesting that the β-*p*-nitrophenylserine obtained by Method 3 was not the same as that from Method 2. Since the Erlenmeyer β-phenylserine has been shown to be of the *threo* configuration, Method 3 was considered to give the *erythro* form. However, the attempt to show non-identity of the two acids and to correlate their configurations with the chloramphenicols by microbiological activities was later reported to be unsatisfactory since the activity difference was too small. The N-dichloroacetyl derivatives were then prepared, but the melting points were the same and no mixed melt was reported.[9] The N-dichloroacetyl-β-*p*-nitrophenylserine prepared in the manner of Method 1 has since been found to have no microbiological activity *vs. S. sonnei*. Since this substance can be shown to be the *threo* modification, it follows that Billet's hope of assigning configuration on the basis of anticipated differing microbiological activities and on the assumption that these must parallel the chloramphenicol activities, must fail.

We have investigated each method of preparation and have been able to demonstrate by chemical methods that the products of Methods 3 and

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[1] Parke, Davis & Co. registered trademark for chloramphenicol.

[2] M. C. Rebstock, *et al.*, This Journal, **71**, 2460 (1950).

[3] D. W. Woolley, *J. Biol. Chem.*, **185**, 293 (1950).

[4] D. Billet, *Compt. rend.*, **230**, 1358 (1950).

[5] C. F. Huebner and C. R. Scholz, This Journal, **73**, 2089 (1951).

[6] C. E. Dalgliesh, *J. Chem. Soc.*, 90 (1949).

[7] E. D. Bergmann, *et al.*, *Compt. rend.*, **231**, 361 (1950).

[8] D. Billet, *ibid.*, **230**, 1074 (1950).

[9] D. Billet, *ibid.*, **231**, 293 (1950).

4 are identical and diastereoisomeric with the product of Method 1. We have been unable to obtain a satisfactory product from direct nitration of β-phenylserine as reported by Billet[4] (Method 2).

The amino acids themselves cannot be distinguished satisfactorily by melting point determination. Each isomer has about the same melting point and there is little depression when mixed. Conversion to the ethyl esters gave derivatives with distinctive melting points.

An ethyl β-*p*-nitrophenylserinate (*erythro*), m.p. 115–116°, is obtained in Method 4 by hydrolysis of the Schiff base which is the initial product. The use of equivalent amounts of *p*-nitrobenzaldehyde and ethyl glycinate was found to improve the yield of condensation product to 66%. Further hydrolysis of the ester produces a β-*p*-nitrophenylserine (*erythro*) which can be esterified to the same ester. The β-*p*-nitrophenylserine (*threo*) from Method 1 gave an ethyl ester melting at 132–133°. This higher-melting ester was also obtained from the diastereoisomer of m.p. 115° by thionyl chloride inversion of the N-acetate. Esterification of the β-*p*-nitrophenylserine from Method 3 gave the ester (*erythro*) melting at 115°, identical with that from Method 4.

The ethyl ester (*erythro*) from Method 4 was treated with methyl dichloroacetate and then with acetic anhydride to produce ethyl N-dichloroacetyl-O-acetyl-β-*p*-nitrophenylserinate (*erythro*), m.p. 85–86°. This was compared with the corresponding compound (*threo*), m.p. 126–127°, obtained from Erlenmeyer's *threo*-β-phenylserine by the same reactions followed by nitration. The products were not identical, but on alkaline hydrolysis yielded the same product, m.p. 183–184°, which is believed to be ethyl α-dichloroacetamido-*p*-nitrocinnamate. Since, in this product, all asymmetry is lost, it could be expected from either diastereoisomer. A second product of the hydrolysis of the 126–127° form was *threo*-N-dichloroacetyl-β-*p*-nitrophenylserine, m.p. 187–189°. Huebner and Scholz have described this method of obtaining N-dichloroacetyl-β-*p*-nitrophenylserine, m.p. 173–175°, and have also obtained and identified the other product of hydrolysis as ethyl α-dichloroacetamido-β-*p*-nitrocinnamate, m.p. 151–155°.

The methods of β-*p*-nitrophenylserine production which involve condensation of *p*-nitrobenzaldehyde with ethyl glycinate thus are shown to yield products of the same diastereoisomeric form which differ from the products of nitration of known *threo*-β-phenylserine derivatives. They are, therefore, assigned the *erythro* configuration.

We are indebted to Dr. George Rieveschl for his interest and support, to Dr. J. M. Vandenbelt for ultraviolet absorption data and to Mr. C. E. Childs, Miss Virginia Pawlik and Mrs. Geraldine Koch for the microanalyses.

ADDED IN PROOF.—Since this note was submitted, the question of the stereochemistry of the β-*p*-nitrophenylserines has been the subject of publications by several groups. The results are not entirely in accord. M. Kopp, *et al.*, *Compt. rend.*, **233**, 527 (1951), have concluded from a chemical investigation that Method 4 leads to the *erythro* form, while E. D. Bergmann, *et al.*, *J. Chem. Soc.*, 2673 (1951), reach the opposite conclusion. D. Molho and L. Molho-Lacroix, *Compt. rend.*, **233**, 1067 (1951), have obtained microbiological evidence of the *erythro* configuration for the product of Method 3 and D. Billet and C. Marnay, *ibid.*, **233**, 961 (1951), support the *erythro* assignment to Method 4 while reporting a modification of the method to yield what is claimed to be the *threo* form. Unfortunately, much of the disagreement is supported by experiment not yet reported in detail or by materials not completely characterized.

Experimental

Ethyl β-*p*-Nitrophenylserinate.—The β-*p*-nitrophenylserines were esterified with absolute ethanol and anhydrous HCl and the liberated amino esters crystallized from aq. ethanol; *threo*, m.p. 132–133°; *erythro*, m.p. 115–116°.

Anal. Calcd. for $C_{11}H_{14}N_2O_5$: C, 51.96; H, 5.55; N, 11.02. Found: *threo:* C, 52.24; H, 5.48; N, 11.00. *erythro:* C, 52.16; H, 5.57; N, 10.95.

Inversion of *erythro*-β-*p*-Nitrophenylserinate.—The *erythro* ester was acetylated with acetic anhydride to the N-acetyl derivative, m.p. 158–159°.

Anal. Calcd. for $C_{13}H_{16}N_2O_6$: C, 52.70; H, 5.44; N, 9.46. Found: C, 52.78; H, 5.50; N, 9.54.

The N-acetate (12 g.) was added during ten minutes to 60 ml. of thionyl chloride. After 40 minutes at room temperature, the mixture was treated cautiously with 120 ml. of water and heated for 1.5 hours on the steam-bath. The chilled solution was neutralized with ammonium hydroxide and the precipitated amino acid separated. The amino acid thus obtained was converted to the ethyl ester, 7.1 g., identical by mixed melting point with the ethyl *threo*-β-*p*-nitrophenylserinate (m.p. 132–133°).

Ethyl N-Dichloroacetyl-O-acetyl-β-*p*-nitrophenylserinate.—The ethyl *erythro*-β-*p*-nitrophenylserinate was treated in methanol solution with methyl dichloroacetate and the product acetylated with acetic anhydride. The acetate melted at 86–87° after crystallization from aq. ethanol.

Anal. Calcd. for $C_{15}H_{16}N_2O_7Cl_2$: C, 44.24; H, 3.96; N, 6.88. Found: C, 44.04; H, 4.06; N, 6.62.

The corresponding *threo* derivative was prepared by the procedure of Huebner and Scholz[5] and melted at 126–127°.

Anal. Found: C, 44.27; H, 4.06.

Each diastereoisomer on treatment with NaOH in acetone at 0° gave ethyl α-dichloroacetamido-*p*-nitrocinnamate, m.p. 183–184°; λ_{max} (in H_2O) 310, $E = 16600$; λ_{max} (in OH^-) 362, $E = 14800$. A mixture of the two showed no melting point depression.

Anal. Calcd. for $C_{13}H_{12}N_2O_5Cl_2$: C, 44.97; H, 3.49. Found: C, 45.14, 45.01; H, 3.69, 3.72.

RESEARCH LABORATORIES
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RECEIVED SEPTEMBER 27, 1951

Preparation of Mo_3Ge and Determination of Its Structure[1]

BY ALAN W. SEARCY, ROBERT J. PEAVLER AND H. J. YEARIAN

In a brief note Wallbaum[2] reported the structures of a number of germanides of transition metals. His note is almost the only report in the literature of this series of compounds. The correspondence in composition and in structure of many of these germanides to silicides of the same elements is of particular interest.

The compounds Mo_3Si,[3,4] Cr_3Si,[5] V_3Si,[6] Cr_3Ge[2]

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[1] This research was supported by the Office of Naval Research.

[2] H. J. Wallbaum, *Naturwissenschaften*, **32**, 76 (1944).

[3] L. Brewer, A. W. Searcy, D. H. Templeton and C. H. Dauben, *J. Am. Ceram. Soc.*, **33**, 291 (1950).

[4] D. H. Templeton and C. H. Dauben, *Acta Cryst.*, **3**, 261 (1950).

[5] B. Boren, *Arkiv Kemi, Mineral. Geol.*, 11a (no. 10), 1 (1933); *Strukturbericht*, **3**, 628 (1937).

[6] H. J. Wallbaum, *Z. Metallkunde*, **31**, 362 (1939).

and V$_3$Ge[2] have been prepared and are all isomorphous. It seemed of interest to attempt the preparation of Mo$_3$Ge.

Samples of molybdenum and germanium powders in atomic ratios of approximately three to one were heated for several hours near 1000° to effect equilibrium. X-Ray diffraction patterns were then obtained with a General Electric powder camera. Filtered copper Kα radiation was used (α_1 = 1.540522 Å., α_2 = 1.544367 Å.). A sample having the over-all composition MoGe$_{0.33}$ gave a very faint molybdenum pattern and the strong pattern of a cubic phase. A sample of composition MoGe$_{0.37}$ gave a strong pattern of the cubic phase and faint lines of a phase that we have shown to be MoGe$_{0.67 \pm 0.03}$. The composition of the cubic phase, therefore, is MoGe$_{0.35 \pm 0.03}$, or Mo$_3$Ge, with no observable solid solution range.

Values of the cell constant *a* obtained from different values of *d/n* (the distance between crystallographic planes) were plotted against $\cos^2 \theta \cot \theta$, where θ is the angle of reflection of the X-ray beam. The plot was extrapolated to $\theta = 90°$ to obtain the best value of *a* from each photograph. The diffraction patterns of two different samples containing Mo$_3$Ge in equilibrium with molybdenum yielded $a = 4.9330 \pm 0.0003$ Å. and $a = 4.9329 \pm 0.0006$ Å. A pattern of Mo$_3$Ge in equilibrium with MoGe$_{0.67}$ yielded $a = 4.9332 \pm 0.0003$ Å. Variation of the lattice constant with composition is within the uncertainties in the measurements, strengthening the conclusion that Mo$_3$Ge has no appreciable solid solution range.

The density of a small, porous sample of Mo$_3$Ge was determined from measurements of its apparent weight in air and in water. This experimental density was 9.7 ± 0.4 g. cm.$^{-3}$; the density calculated assuming six molybdenum atoms and two germanium atoms per unit cell of the cubic lattice was 9.97 ± 0.01 g. cm.$^{-3}$.

Values for *d/n* calculated for lines from the diffraction pattern of Mo$_3$Ge corresponded very closely to those reported by Templeton and Dauben[4] for Mo$_3$Si, although six of the weaker lines of the Mo$_3$Si pattern were missing from the Mo$_3$Ge pattern. The two phases are obviously isomorphous. Table I lists the *hkl* assignments, *d/n* values, and calculated and visual intensities for Mo$_3$Ge. The calculated intensities were reduced to the same arbitrary scale used by Templeton and Dauben in their determination of the structure of Mo$_3$Si, and their values for Mo$_3$Si were included in the table for comparison. The intensities calculated for Mo$_3$Ge agree satisfactorily with the intensities observed. The six lines observed in the Mo$_3$Si pattern, but not observed in the Mo$_3$Ge pattern, all have very low calculated intensities for Mo$_3$Ge. Thus Mo$_3$Ge, like Mo$_3$Si, belongs to space group O$_h^3$–Pm3n and has the β-tungsten[7] structure. The positions of the atoms are: two Ge in (a) at 0, 0, 0; $^1/_2$, $^1/_2$, $^1/_2$; and six Mo in (c) at $^1/_4$, 0, $^1/_2$; $^1/_2$, $^1/_4$, 0; 0, $^1/_2$, $^1/_4$; $^3/_4$, 0, $^1/_2$; $^1/_2$, $^3/_4$, 0; 0, $^1/_2$, $^3/_4$.

Each germanium atom in Mo$_3$Ge is surrounded by 12 molybdenum atoms at 2.75 Å. Each molybdenum atom has two molybdenum atoms at 2.46 Å., four germanium atoms at 2.75 Å. and eight molybdenum atoms at 3.02 Å.

TABLE I

DIFFRACTION DATA FOR Mo$_3$Ge

vs, very strong; s, strong; m, medium; w, weak.

hkl	Mo$_3$Ge *d*	Mo$_3$Ge Visual	Mo$_3$Ge Calcd.	Mo$_3$Si (T + D)[4] Calcd.
110	3.4724	w$^-$	5	36
200	2.4557	w	45	25
210	2.1993	vs	163	183
211	2.0031	s	96	58
220	....	Absent	<1	3
310	....	Absent	1	7
222	1.4215	w	17	25
320	1.3663	w$^+$	34	26
321	1.3167	m	44	26
400	1.2323	w$^-$	21	16
330 411	....	Absent	1	4
420	1.1024	w	13	7
421	1.0755	m	34	33
332	1.0506	w$^-$	12	7
422	....	Absent	<1	2
431 510	....	Absent	<1	6
432 520	0.9158	s	46	43
521	0.9004	m$^-$	23	13
440	0.8720	m$^+$	30	22
433 530	....	Absent	<1	5
442 600	0.8221	w$^+$	20	12
610	0.8110	m	25	27
532 611	0.8002	s	63	39

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RECEIVED JULY 26, 1951

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[7] H. Hartmann, F. Ebert and O. Bretschneider, *Z. anorg. Chem.*, **198**, 116 (1931).

The Purification and Identification of 1-Methylnaphthalene

BY MILTON D. SOFFER AND ROBERTA A. STEWART[1]

The inefficacies of conventional methods for the liberation of 1-methylnaphthalene from its usual impurity, the 2-methyl isomer, have been pointed out recently by Morrell, Pickering and Smith.[2] The best method in the literature[2,3,3b] involves a rather tedious process, *i.e.*, sulfonation, conversion of the sulfonic acids to their *p*-toluidine salts, frac-

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[1] Department of Chemistry, Wellesley College, Wellesley, Mass.

[2] S. H. Morrell, G. B. Pickering and J. C. Smith, *J. Inst. Petroleum*, **34**, 677 (1948).

[3] (a) G. T. Morgan and E. A. Coulson, *J. Soc. Chem. Ind.*, **53**, 73 (1934); (b) after this article was submitted it was brought to our attention that a method involving distillation of the hydrocarbon under special conditions in the presence of 5-ethylnonanol as an azeotropic agent was reported by J. Feldman and M. Orchin; Abstracts of Papers, 117th Meeting, American Chemical Society, Chicago, Ill., September 3 to 8, 1950.

tional crystallization, hydrolysis of the salt, and desulfonation of the acid.

Although 1-methylnaphthalene picrate is listed in reference books as a suitable derivative for identification of the hydrocarbon, the substance cannot be obtained directly from the 1-methylnaphthalene usually available commercially.[4] The constant melting picrate obtained in the regular way is apparently[2] a 1:1 addition product of the picrates of the two isomeric hydrocarbons. Consequently the picrate cannot be used generally for purposes of identification and purification. The styphnate is also unsatisfactory.

In the course of a separate investigation we have shown that this limitation does not apply to the addition products with 1,3,5-trinitrobenzene and 2,4,7-trinitrofluorenone. These derivatives serve well for identification, and yield the pure hydrocarbon by chemical methods or simply by perfusion through alumina The regenerated hydrocarbon gives directly the authentic derivatives with picric or styphnic acid, trinitrobenzene or trinitrofluorenone.

We wish to express our appreciation to the Research Corporation for a grant supporting this work.

Experimental

Treatment of several representative batches of 1-methylnaphthalene[4] with picric acid in methanol or ethanol, in the usual way, gave the 1:1 "compound"[2] of the **mixed picrate**, whose final melting point, 123.5–124°, was unchanged by further recrystallization. The melting point frequently mentioned in the literature[2] is 121–123°. The authenticated melting point of the picrate of 1-methylnaphthalene is 141.5°, and that of the 2-isomer is 116–117°.[2]

Attempts to prepare the **styphnate** from the same hydrocarbon[4] did not give a homogeneous product. In a typical case, equimolar quantities of styphnic acid and the hydrocarbon were boiled in methanol to effect solution. The yellow solid which separated on cooling melted at 114–120° and dissociated with erratic broadening of the melting range (*ca.* 103–145°) on recrystallization from methanol, 95% ethanol, or acetic acid. The recorded[2] melting points of the styphnates of 1- and 2-methylnaphthalene are 134–135° and 129.5°, respectively.

The melting point of the **trinitrobenzene derivative** prepared from 10.7 g. (0.053 mole) of the commercial hydrocarbon[4] and 7.81 g. (0.055 mole) of 1,3,5-trinitrobenzene in 50 ml. of 95% ethanol was constant (153–153.5°) after five recrystallizations from methanol. The melting points in the literature[2] are 147° and 153.5–154.5° for the 1-methyl isomer and 123° and 124° for the 2-methyl isomer.

The same hydrocarbon,[4] 0.90 g. (0.00635 mole), with 2.0 g. (0.00635 mole) of 2,4,7-trinitrofluorenone[5] in hot glacial acetic acid gave the pure **trinitrofluorenone derivative**, constant melting (163–164°) orange needles, after five recrystallizations from glacial acetic acid.

Anal. Calcd. for $C_{24}H_{15}O_7N_3$ (1:1 complex); C, 63.0; H, 3.3; N, 9.2. Found: C, 62.8, 63.0; H, 4.0, 3.9; N, 9.5, 9.2.

The derivative dissociated completely when it was kept for 28 hours at 1 mm. and 80°. The analytical sample was unchanged by drying in vacuum at room temperature for two weeks.

The **pure 1-methylnaphthalene** was regenerated from the trinitrofluorenone or trinitrobenzene derivatives by passing a dry benzene solution through a 15-inch column of activated alumina and washing with benzene (to which petroleum ether (35–60°) was added in the case of the trinitrobenzene derivative) until the colored band of the nitro compound moved down near the end of the column. From 0.27 g. of the trinitrofluorenone derivative and 0.18 g. of the trinitrobenzene derivative the regenerated hydrocarbon was obtained in quantitative yield, 0.08 and 0.07 g., respectively.

Another sample of the trinitrobenzene derivative (2.7 g.) was treated with tin and acetic–hydrochloric acids essentially as described by Orchin.[5] The solution was extracted with ether and benzene and the combined extracts after washing successively with dilute hydrochloric acid, strong alkaline sodium hyposulfite, water, dilute hydrochloric acid and water, gave the pure 1-methyl isomer in quantitative yield (1.1 g.).

Samples of the hydrocarbon regenerated from the trinitrobenzene derivative were treated separately in the usual way with picric acid, styphnic acid, and trinitrobenzene in boiling methanol, and with trinitrofluorenone in hot glacial acetic acid. In each case the derivative separated directly in pure condition; the melting points were 141–141.5°, 134.5–135°, 154–154.5° and 163–164°, respectively, and were not changed by recrystallization. The melting point of this trinitrofluorenone derivative was not changed by admixture with the trinitrofluorenone derivative prepared direct from the commercial hydrocarbon.

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RECEIVED MAY 18, 1951

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[4] Eastman Kodak Co., Rochester, N. Y.

[5] M. Orchin and E. O. Woolfolk, THIS JOURNAL, **68**, 1727 (1946); M. Orchin, L. Reggel and E. O. Woolfolk, *ibid.*, **69**, 1225 (1947).

Enrichment of Tin Activity Through the Szilard–Chalmers Separation

BY HERTA SPANO[1] AND MILTON KAHN

We wish to report that tetraphenyltin is a suitable compound for the enrichment of tin activity through the Szilard–Chalmers reaction. Solid tetraphenyltin was irradiated with slow neutrons, dissolved in benzene and extracted with various aqueous solutions. In nearly every case a large fraction of the tin activity appeared in the aqueous phase associated with a small amount of inactive tin. The results are summarized in Table I.

TABLE I

Expt.	Aqueous solution	Enrichment factor[a]	Sn activity in aqueous phase, %
1	H_2O	113	4
2	3.0 *f* HCl	2200	40
3	6.0 *f* HCl	2700	48
4	1.0 *f* NaOH	2800	50

[a] Specific activity of tin in aqueous phase divided by specific activity of tin in tetraphenyltin before extraction.

Experimental

Tetraphenyltin obtained from Eastman Kodak Co. was used without further purification. Eight hundred-milligram samples of tetraphenyltin were irradiated in the thermal column of the Los Alamos Fast Reactor for two hours. Each sample was transferred to a 150-ml. beaker, and dissolved in 100 ml. of thiophene-free benzene. This solution was then transferred to a 125-ml. separatory funnel and shaken for five minutes at room temperature with 20 ml. of an aqueous solution. The aqueous phase was washed with 50 ml. of benzene. The tin activity in both the extracted benzene phase and the aqueous solution was determined. Also, the aqueous phase was analyzed for total tin. In each instance no more than 0.04 mg. of tin was found in the aqueous phase. It turned out that the amount of tin detected in the aqueous phase, in each case, was independent of whether or not the tetraphenyltin had been irradiated.

In all experiments the fraction of the total tin activity recovered in each phase was computed on the basis of the tin activity found in a 36-mg. sample of tetraphenyltin

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[1] This paper is a portion of the dissertation presented by Herta Spano in fulfillment of the requirements for the Master's Degree in the Graduate School of the University of New Mexico, June, 1951.

which was alongside the 800-mg. samples during each irradiation.

Since the success of the Szilard–Chalmers reaction is known to be dependent on the level of the γ-radiation in the pile it was desirable that all samples be irradiated under the same conditions.[2] The tetraphenyltin samples used in experiments 1 and 2 were alongside each other in the pile during the irradiation as were the samples used in experiments 3 and 4. It is believed that the γ-fluxes during these two irradiations were approximately the same because the beta activity of the samples used in experiments 3 and 4 was only 15% higher than that of the samples used in experiments 1 and 2.

The β-activity of the 1.1-day Sn^{121} was detected in all experiments. During the two-hour irradiation the activities of Sn^{113} and Sn^{123} produced are negligible compared to that of Sn^{121}. The 2.7-year Sb^{125} activity that is produced through decay of the 10-minute Sn^{125} is also negligible compared to the Sn^{121} activity. The tin was precipitated as stannic phenylarsonate,[3] suspended in 5 ml. of 95% alcohol and then prepared for counting by filtration on a tared, 24 mm. diameter, Whatman #50 filter paper, dried for 30 minutes at 110°, and weighed. The counting samples measured 14 mm. in diameter and were mounted on 2 × 2.5 in. cardboard cards with scotch tape placed directly over the sample. These cards were placed in a holder which fixed the position of the sample relative to an Amperex #100 C Geiger–Muller tube. All counting samples had activities within the range from 600 to 6000 counts per minute, and in this range the response of the counter was linear. The thickness of the samples, which was of the order of 28 mg./cm.^{2}, varied as much as 2 mg./cm.^{2}, necessitating corrections for self-absorption of the β-particles. The self-absorption correction amounted to a 1.15% increase in the total counting rate of a sample for each milligram increase in sample weight.

In order to determine the tin activity in the aqueous phase a 5-ml. aliquot was warmed slightly to remove traces of benzene, and then treated with a drop of liquid bromine so that all the tin present would be in the stannic state. The excess bromine was removed by gentle heating, and 1 ml. of a solution of stannic chloride containing 10 mg. of tin per ml. was added. The tin was precipitated as stannic hydroxide which was then dissolved in a minimum of 6 *f* hydrochloric acid. One-half ml. of 6 *f* hydrochloric acid was added in excess, and the sample diluted to 5 ml. with water. The sample was heated to 90° and then 5 ml. of a saturated aqueous solution of phenylarsonic acid was added. After a digestion period of ten minutes at 90°, the sample was cooled, allowed to stand at room temperature for 15 minutes, and then mounted for counting. The percentage of tin in the precipitate formed under these conditions was equal to that calculated from the formula of stannic phenylarsonate within a probable error of 1%.

The tin activity in the benzene phase was determined by evaporating an aliquot to dryness, ashing the tetraphenyltin residue with concentrated sulfuric acid and 30% hydrogen peroxide, and finally precipitating the tin as stannic phenylarsonate which was then mounted for counting. The tin activity in the 36-mg. sample of tetraphenyltin was determined in the same way.

In all the experiments only about 80% of the total tin activity was recovered. It turned out that approximately 80% of the activity lost was adsorbed on the walls of the beaker in which the irradiated solid tetraphenyltin was originally dissolved. In one experiment[4] an irradiated sample of tetraphenyltin was dissolved directly in a separatory funnel prior to extraction with 3 *f* hydrochloric acid and accordingly a larger enrichment factor (3400) and a higher yield (61%) were obtained. These results suggest the formation of tin radiocolloids in benzene.

The total tin present in the aqueous phase was determined colorimetrically by observing the molybdenum-blue color produced by the action of stannous tin on a molybdate reagent.[5] After reduction to the stannous state the color produced by the tin present in an aliquot of the aqueous phase was compared, visually, with that produced in several standard solutions of tin.

Acknowledgment.—We wish to express our appreciation to Dr. Roderick W. Spence and Mr. James E. Sattizahn, Jr., of the Los Alamos Scientific Laboratories for irradiation of the samples of tetraphenyltin.

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[2] R. R. Williams, *J. Phys. Colloid Chem.*, **52**, 603 (1948).

[3] E. G. Meyer, Ph.D. Thesis, University of New Mexico, 1950.

[4] On the basis of the β-activity of this irradiated sample, the γ-flux during the irradiation of this sample was the same as that during the irradiation of the samples used in experiments 3 and 4.

[5] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," 3rd. ed., D. Van Nostrand Co., New York, N. Y., 1949, p. 217.

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UNIVERSITY OF NEW MEXICO
ALBUQUERQUE, NEW MEXICO

RECEIVED AUGUST 9, 1951

COMMUNICATIONS TO THE EDITOR

THE SYNTHESIS OF BUTATRIENE[1]

Sir:

Butatriene has been synthesized in high yield by the action of powdered zinc on 1,4-dibromobutyne in purified diethylene glycol diethyl ether at 70°. The reaction product was collected as a low boiling liquid in a Dry Ice–acetone trap, or as a solid in a liquid nitrogen trap. The material polymerized upon being warmed to room temperature in the absence of air and with hydroquinone or other inhibitors present. The monomer showed negative tests with acetylenic hydrogen reagents such as alkaline mercuric iodide. With bromine in carbon tetrachloride it gave 1,2,3,4-tetrabromobutene-2 (80% yield), m.p. 68–69.5°, identical with an authentic sample prepared by bromination[2] of 1,4-dibromobutyne-2.

The butatriene exhibited the following physical properties: C/H ratio on two different samples, 92.29/7.71 and 91.82/8.18; mol. wt. (Dumas method at 250 mm. pressure), 52.6; mass spectrum (relative intensities): mass 52 (100), mass 51 (72), mass 50 (54); u.v. max. (95% ethanol), 241 mμ (20,300), apparent max. 310 mμ (250). In the infrared[3] (gas, 100 mm., 10 cm. cell), strong bands were shown at 2990, 1708, 1610, and 860 cm.$^{-1}$ (broad); medium bands at 2030, 1358, 1206, and 1065 cm.$^{-1}$ (broad).

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RECEIVED NOVEMBER 23, 1951

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[1] Supported in part by the Research Corporation.

[2] A. Valette, *Ann. chim.*, [12] **3**, 644 (1948).

[3] For aiding in obtaining the data we wish to thank Dr. David Eggers, who is now working on a more detailed interpretation of the infrared spectrum.