

TABLE I
 PROPOXYMETHYL ALKYL (OR PHENYL) KETONES, C₃H₇OCH₂COR 2,4-DINITROPHENYLHYDRAZONES

C ₃ H ₇ :	R	Yield, %	B. p., (cor.) mm.	n _D ²⁰	d ₄ ²⁰	Molec. refract.		Carbon, %		Hydrogen, %		M. p., °C. (cor.)	Nitrogen, %		
						Calcd.	Found	Calcd.	Found	Calcd.	Found		Calcd.	Found	
<i>n</i> -	-CH ₃	52	49 ^a	6	1.4052	0.9020	31.56	31.55	62.04	61.88	10.41	10.36			
<i>i</i> -	-CH ₃	48	35	10	1.4004	.8918	31.56	31.59	62.04	62.11	10.41	10.40	144	18.92	19.03
<i>n</i> -	-C ₂ H ₅	46	56	4	1.4122	.8940	36.18	36.17	64.57	64.26	10.84	10.68			
<i>i</i> -	-C ₂ H ₅	41	47	11	1.4082	.8875	36.18	36.18	64.57	64.24	10.84	10.98	103	18.06	18.16
<i>n</i> -	<i>n</i> -C ₃ H ₇	64	64	4	1.4155	.8858	40.80	40.80	66.62	66.42	11.18	11.02			
<i>i</i> -	<i>n</i> -C ₃ H ₇	42	56	8	1.4120	.8786	40.80	40.82	66.62	66.72	11.18	11.20	98	17.28	17.39
<i>n</i> -	<i>i</i> -C ₃ H ₇	35	79	60	1.4147	.8847	40.80	40.80	66.62	66.49	11.18	11.19			
<i>i</i> -	<i>i</i> -C ₃ H ₇	8	42	6	1.4095	.8790	40.80	40.56	66.62	65.86	11.18	11.02	89	17.28	17.43
<i>n</i> -	<i>n</i> -C ₄ H ₉	51	81	12	1.4210	.8815	45.42	45.44	68.31	68.02	11.47	11.36			
<i>i</i> -	<i>n</i> -C ₄ H ₉	37	63	7	1.4196	.8761	45.42	45.38	68.31	68.03	11.47	11.51	78	16.57	16.66
<i>i</i> -	<i>i</i> -C ₄ H ₉	25	56	5	1.4138	.8674	45.42	45.54	68.31	68.01	11.47	11.57	95	16.57	16.65
<i>i</i> -	<i>s</i> -C ₄ H ₉	11	50	5	1.4165	.8763	45.42	45.33	68.31	67.70	11.47	11.17	61	16.57	16.72
<i>n</i> -	<i>n</i> -C ₅ H ₁₁	48	120	45	1.4240	.8783	50.03	50.04	69.72	69.47	11.70	11.49	73	15.91	16.08
<i>i</i> -	<i>n</i> -C ₅ H ₁₁	45	83	8	1.4209	.8709	50.03	50.12	69.72	69.83	11.70	11.89	77	15.91	16.07
<i>n</i> -	<i>i</i> -C ₅ H ₁₁	46	111	26	1.4230	.8726	50.03	50.02	69.72	69.43	11.70	11.56	79	15.91	16.36
<i>i</i> -	<i>i</i> -C ₅ H ₁₁	30	83	9	1.4189	.8691	50.03	50.02	69.72	69.36	11.70	11.78	82	15.91	16.03
<i>n</i> -	-C ₆ H ₅	37	118	6	1.5150	1.0333	51.71 ^b	51.94	74.13	73.87	7.92	7.87			
<i>i</i> -	-C ₆ H ₅	40	112	6	1.5129	1.0290	51.71 ^b	51.97	74.13	74.01	7.92	7.77			

^a Gauthier [*Ann. chim. phys.*, [8] 16, 289 (1909)] reported b. p. 145° (732 mm.); we record b. p. 150° (763 mm.).

^b Includes 0.65 for exaltation due to C₆H₅CO grouping [*J. prakt. Chem.*, [2] 84, 35 (1911)].

viscous reaction mixture to continue. Hydrolysis of the adduct was accomplished with cold hydrochloric acid, usually yielding a deeply red-colored solution. After repeated fractionation, the ketones are stable, colorless liquids with characteristic odor. They decompose slightly when heated to their respective boiling points at atmospheric pressure.

Summary

The synthesis is reported of sixteen new keto ethers containing either the normal or isopropoxy grouping.

AUSTIN, TEXAS

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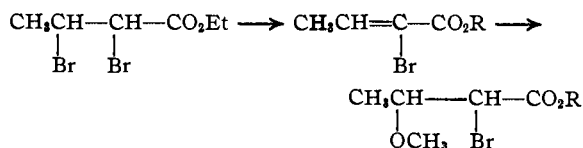
NOTES

Synthesis of α -Bromo- β -methoxy-*n*-butyric Acid

BY HERBERT E. CARTER AND LUMAN F. NEY

As an intermediate in the synthesis of threonine West and Carter¹ used the mixture of α -bromo- β -methoxy-*n*-butyric acids obtained by brominating a mercuration product of crotonic acid. This mixture of bromomethoxybutyric acids contains approximately 50% of the threonine² precursor. Recently Wood and du Vigneaud³ reported the conversion of ethyl α,β -dibromopropionate to ethyl α -bromo- β -ethoxypropionate by the action of sodium ethylate. It seemed probable that ethyl α -bromo- β -methoxy-

n-butyrate might be prepared from ethyl α,β -dibromo-*n*-butyrate in a similar manner. Therefore we have made a study of the reactions



The reaction of ethyl α,β -dibromo-*n*-butyrate with one mole of sodium methylate gives ethyl α -bromocrotonate together with a small amount of ethyl α -bromo- β -methoxy-*n*-butyrate. However, in the presence of slightly larger quantities of sodium methylate the dibromo ester is converted into the bromomethoxy ester in yields of 80–90%. Ethyl α -bromocrotonate also gives an excellent yield of bromomethoxy ester when treated with sodium methylate and hence may be considered an intermediate in the above reaction.

(1) West and Carter, *J. Biol. Chem.*, **119**, 109 (1937).

(2) α -Amino- β -hydroxy-*n*-butyric acids exist in two racemic forms, *dl*-threonine and *dl*-allo-threonine. Threonine has the same spatial configuration as does threose, hence the name [Meyer and Rose, *J. Biol. Chem.*, **115**, 721 (1936)]. The second form was designated as allothreonine by West and Carter¹ to express its relation to threonine.

(3) Wood and du Vigneaud, *ibid.*, **134**, 413 (1940).

The approximate composition of the product was determined by hydrolyzing the ester, aminating the bromo acid, and separating the mixture of aminomethoxybutyric acids thus obtained through the benzoyl derivatives. The yield of benzoylamino-methoxybutyric acid was 50–55% calculated on the ethyl crotonate originally used. Approximately 85% of the product consisted of benzoyl-*dl*-O-methylallothreonine. This series of reactions therefore provides an excellent method for the preparation of allothreonine, while the mercuration procedure remains the preferable method for the synthesis of threonine. It is interesting to note that the addition of sodium methylate to ethyl α -benzoylamino-crotonate gives mainly the threonine isomer in marked contrast to the behavior of ethyl α -bromocrotonate.

Experimental

Each of the reactions was repeated a number of times. Typical results are described below.

Ethyl α,β -dibromo-*n*-butyrate.⁴—Ethyl crotonate (570 g. or 5 moles) was placed in a 5-liter three-necked flask fitted with a mechanical stirrer and a dropping funnel. The flask was cooled in an ice-bath and 800 g. (5 moles) of bromine was added slowly with vigorous stirring over a period of seventy-five minutes. The reaction mixture was stirred for fifteen minutes after the bromine addition was completed. The product was distilled under reduced pressure giving 1300 g. (95% yield) of ethyl α,β -dibromo-*n*-butyrate; b. p. 103–104° (17 mm.).

Ethyl α -Bromo- β -methoxy-*n*-butyrate.—The reaction of ethyl α,β -dibromobutyrate with sodium methylate was carried out at temperatures ranging from –5 to 25°. No significant difference in the composition of the product was observed over this range.

Ethyl α,β -dibromo-*n*-butyrate (1096 g. or 4 moles) was placed in a 5-liter three-necked flask fitted with a stirrer, dropping funnel and calcium chloride tube. The flask was cooled in an ice-bath and a solution of 115 g. (5 moles) of sodium in 2000 cc. of absolute methyl alcohol was added over a period of seventy-five minutes. The stirring was continued for one hour (with cooling). The reaction mixture was then poured into 5 liters of cold water containing 200 cc. of concentrated hydrochloric acid. The ester layer was separated. The aqueous layer was extracted with three 1-liter portions of ether and the ether extracts were combined with the ester layer. This solution was washed with a saturated solution of calcium chloride, then with water and was dried over sodium sulfate. The ether was removed and the residue was distilled under reduced pressure. The yield of ethyl α -bromo- β -methoxy-*n*-butyrate was 720–810 g., 80–90%; b. p. 90–100° (18 mm.).

α -Bromo- β -methoxy-*n*-butyric Acid.—The bromomethoxy ester (1125 g.) and 1 liter of 0.5 *N* sodium hydroxide were placed in a 5-liter three-necked flask fitted with a

stirrer, dropping funnel and thermometer. The flask was cooled in an ice-bath and vigorously stirred while 1 liter of 5 *N* sodium hydroxide was added at such a rate that the temperature of the reaction mixture was maintained at 15–20°; the addition required about one hour. The ice-bath was then removed and the stirring was continued for thirty minutes. The flask was again cooled while 500 cc. of concentrated hydrochloric acid was added slowly. The bromo acid layer was separated. The aqueous layer was extracted three times with 1-liter portions of ether. The combined ether extracts and bromo acid were washed once with cold water and dried over sodium sulfate. The ether was distilled and water was removed under reduced pressure giving a nearly quantitative yield of crude α -bromo- β -methoxy-*n*-butyric acid. The benzoylamino-methoxybutyric acids were prepared from this material as previously described.¹

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The Heat Capacity of Organic Vapors. III. Nitromethane¹

BY THOS. DE VRIES AND BEN. T. COLLINS²

Recently Pitzer and Gwinn³ published values for the heat capacity of nitromethane and from their data calculated the potential of the barrier to rotation about the C–N bond. At that time similar measurements for nitromethane were completed in this Laboratory and since our data are in excellent agreement with those of Pitzer and Gwinn they are published here in confirmation of their results.

Experimental.—A good grade of nitromethane, produced by Commercial Solvents Corporation, was dried over calcium chloride and rectified. Only the middle fraction, approximately 60%, having a boiling range of less than 0.1° was collected for use.

The apparatus and experimental technique described in a previous article⁴ was used. Since the values obtained at atmospheric pressure were so much higher than expected,⁵ it was decided to make measurements at reduced pressures which were held constant to ≈ 2 mm. of mercury pressure. The calibration of the ten-junction thermel at the completion of the research was found to be unchanged.

(1) Abstracted from a thesis to be submitted by B. T. Collins in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Present address: Stanolind Gas and Oil Co., Tulsa, Okla.

(3) Pitzer and Gwinn. *THIS JOURNAL*, **63**, 3313 (1941).

(4) De Vries and Collins. *ibid.*, **63**, 1343 (1941).

(5) E. B. Wilson, Jr., private communication, 1941.

(4) Goss, Ingold and Thorpe, *J. Chem. Soc.*, **123**, 3342 (1923).

The data were corrected for heat loss to the surroundings by plotting the results against the square of the reciprocal rate of flow ($1/F^2$), which has the units (sec./g.)². The intercepts at an infinite rate of flow give the true specific heat for a selected temperature and pressure. Typical results are presented in Table I and a summary of all the data in Table II together with data presented by Pitzer and Gwinn. From three to six determinations were used to obtain the extrapolated values listed in Table II. The length of a run was thirty minutes, the temperature rise varied from 3.5 to 7° and the heat input was usually between 0.026 and 0.038 calorie per second.

TABLE I

TYPICAL RESULTS AND CALCULATIONS FOR SPECIFIC HEAT AT INFINITE RATE OF FLOW (F)

Temp., °C.	P = 0.98		P = 0.50		P = 0.25	
	1/F ²	Specific heat	1/F ²	Specific heat	1/F ²	Specific heat
105	5135	0.348	2357	0.320	1387	0.299
	1658	.319	1192	.304	947	.291
	842	.314	665	.298	686	.286
	0	.307	0	.281	0	.275
130	4006	.346	2940	.335	958	.300
	1997	.327	1527	.315	497	.293
	1161	.317	1089	.307	495	.291
	0	.308	0	.292	0	.283

TABLE II

HEAT CAPACITY OF NITROMETHANE

Units: C_p in cal. per mole per degree, P in atm.

t , °C.	100	105	115	130	133	145	161
$P = 0.98$		18.71	18.63	18.79		18.96	19.11
$P = 0.50$		17.52	17.58	17.82			
$P = 0.25$		16.84	16.97	17.27			
$P = 0$		16.22	16.45	16.81			
$P = 0$	16.11				16.87		
(Pitzer and Gwinn)							
$C_{L+r+vib.}$		15.09	15.37	15.82			
$C_{I.R.}$		1.13	1.08	0.99			
$C_{I.R.}$	1.17				0.98		
(Pitzer and Gwinn)							

The heat capacity contributions from translation, rotation and vibration were calculated by Wilson,⁵ using the spectroscopic data of Wells and Wilson.⁶ The difference ($C_{I.R.}$) between the calculated sum and the experimental values compares well with similar values given by Pitzer and Gwinn, and indicates that the potential barrier is close to but less than 800 cal.

One of the authors (B. T. C.) wishes to thank the Purdue Research Foundation for financial assistance in the form of a research fellowship.

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(6) Wells and Wilson, *J. Chem. Phys.*, **9**, 314 (1941).

Investigations in the 1-Methylphenanthrene Series. III. The Synthesis of 3-Acetyl-1-methylphenanthrene

BY TORSTEN HASSELSTROM AND DAVID TODD

Phenanthrene when subjected to the Friedel-Crafts reaction with acetyl chloride as the active reagent yields 3-acetylphenanthrene and, in smaller amounts, the 2-derivative.¹ Recently Campbell and Todd² provided evidence that the acetyl group in the acetylretene of Bogert and Hasselstrom³ occupies the 3-position. It is of interest to note that when this reaction is applied to 9,10-dihydrophenanthrene⁴ or 9,10-dihydroretene⁵ the resultant product is the 2-derivative, thus pointing to the fact that the alkyl groups apparently do not have a directing influence on the substitution of the phenanthrene nucleus.

Our investigation deals with the acetyl-1-methylphenanthrene, which was prepared from 1-methylphenanthrene through the Friedel-Crafts reaction. The 3-derivative was obtained since the acetyl-1-methylphenanthrene on oxidation with fuming nitric acid yielded mellophanic (1,2,3,5-)acid.

The new phenanthrene was characterized by derivatives. The Beckmann rearrangement of the oxime and subsequent saponification of the acetamine produced the 3-amino-1-methylphenanthrene, which by means of the diazo reaction gave a new phenanthrol, 1-methylphenanthrol-3.

Experimental

3-Acetyl-1-methylphenanthrene (T. H.).—Twenty-five grams of 1-methylphenanthrene⁶ was dissolved in 100 cc. of nitrobenzene and 16 cc. of acetyl chloride. The solution was kept in an ice and salt mixture at 0° and 29 g. of pulverized aluminum chloride was added in two portions at ten minute intervals. After two hours the solution was allowed to come to room temperature and after standing for one hour, the semi-solid dark mass was poured into ice and 100 cc. of concentrated hydrochloric acid. The oily residue, after steam distillation, was treated with norite in methanol solution and yielded 11.5 g. of crystalline material, together with some oil. The acetyl-1-methylphenanthrene was recrystallized from methanol and finally from benzene; m. p. 111.5–112.5° (cor.) of slightly yellowish prisms.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.06; H, 6.02. Found: C, 86.95; H, 6.197 (D. T.); C, 87.37; H, 5.89.

(1) Mosettig and van de Kamp, *THIS JOURNAL*, **52**, 3704 (1930).

(2) Campbell and Todd, *ibid.*, **62**, 1287 (1940).

(3) Bogert and Hasselstrom, *ibid.*, **53**, 3462 (1931).

(4) Burger and Mosettig, *ibid.*, **57**, 2731 (1935).

(5) Nyman, *Am. Acad. sci. Fennicas*, **A41**, No. 5 (1934).

(6) Hasselstrom, *THIS JOURNAL*, **63**, 1164 (1941).

(7) Analysis by Mr. S. Gottlieb, Columbia University, New York, N. Y.

When the reaction was carried out at 0 to 5° and kept at this temperature for about two weeks 30% of 3-acetyl-1-methylphenanthrene together with a small amount of impure material melting at 152–153° (uncor.) was obtained (D. T.).

Picrate of 3-Acetyl-1-methylphenanthrene (T. H.).—Yellow needles, recrystallized from methanol; m. p. 137–137.5° (cor.).

Anal. Calcd. for $C_{23}H_{17}O_3N_3$: N, 9.07. Found: N, 9.35.⁷

The Oxidation of 3-Acetyl-1-methylphenanthrene (D. T.).—Seventy-five hundredths gram of the acetyl compound together with 2 cc. of fuming nitric acid and 3 cc. of water was heated in a Carius bomb tube for one-half hour on the steam-bath. The tube was then sealed and heated for three hours at 190°. One cc. of nitric acid was added and the tube was reheated at 190° for three hours. The solution was evaporated to dryness and the white residue was washed on a filter with 10 cc. of fuming nitric acid. Esterification of the solid with diazomethane and crystallization from methanol gave white needles melting at 109.5–110°. After recrystallization the melting point was 111–112° (uncor.). The ester did not lower the melting point of an authentic sample of the tetramethyl ester of benzene-1,2,3,5-tetracarboxylic acid (m. p. 110.5–111° (uncor.)), m. p. of the mixture being 111–112° (uncor.).

Oxime of 3-Acetyl-1-methylphenanthrene (T. H.).—Recrystallized from ethanol; white needles; m. p. 180.5–181° (cor.).

Anal. Calcd. for $C_{17}H_{15}ON$: N, 5.62. Found: N, 5.44.⁷

3-Acetamino-1-methylphenanthrene (T. H.).—One gram of the oxime of 3-acetyl-1-methylphenanthrene dissolved in 10 cc. of anhydrous ether and 1 g. of phosphorus pentachloride was added slowly to the cooled solution. The temperature was kept at 15–20° during the reaction. The reaction mixture was then washed with water until washings were no more acid to litmus. The ether solution was dried with anhydrous sodium sulfate, the ether evaporated, the solid residue dissolved in ethanol and treated with Norite; yield about 0.14 g. The 3-acetamino-1-methylphenanthrene was recrystallized from ethanol; white needles; m. p. 188.5–189.5° (cor.).

Anal. Calcd. for $C_{17}H_{15}ON$: C, 81.90; H, 6.07. Found: C, 81.98; H, 6.06.⁷

3-Diacetamino-1-methylphenanthrene (T. H.).—0.2 gram of the monoacetyl derivative was refluxed with 5 cc. of acetic anhydride for thirty minutes and 0.2 g. of sodium acetate. The solution was poured into 50 cc. of water and the precipitate recrystallized from methanol; yield, about quantitative, colorless needles; m. p. 162–162.5° (cor.).

Anal. Calcd. for $C_{19}H_{17}O_2N$: C, 78.33; H, 5.88. Found: C, 78.59; H, 6.11.⁷

3-Amino-1-methylphenanthrene (D. T.).—A solution of 0.8 g. of the oxime of 3-acetyl-1-methylphenanthrene in 10 cc. of acetic acid and 5 cc. of acetic anhydride was treated with dry hydrogen chloride for ten minutes. The mixture was diluted with 10 cc. of acetic acid, 10 cc. of concentrated hydrochloric acid, and 1 cc. of water and refluxed for twelve hours. The precipitate which formed on dilution with water was taken up in ether, dried and the amine hydro-

chloride was precipitated with dry hydrogen chloride. This product was heated for several hours with 500 cc. of water, filtered hot, and cooled. The white flocculent precipitate which separated was crystallized from ethanol containing alkali. There was obtained 0.07 g. of glistening plates; m. p. 126–127° (uncor.). Two more crystallizations from ethanol did not change the melting point.

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.91; H, 6.32. Found: C, 86.66, 86.56; H, 6.04, 6.23.

1-Methylphenanthrol-3 (T. H.).—Two grams of 3-amino-1-methylphenanthrene was dissolved in 800 cc. of water containing 8 cc. of concentrated hydrochloric acid and cooled to 2°. A concentrated solution of 1 g. of sodium nitrate was added in portions and the yellow solution allowed to stand in the icebox for one and one-half hours. After addition of 2.5 g. of urea the turbid solution was slowly heated to boiling and the precipitate 1.89 containing a reddish resin filtered off and suspended in a dilute potassium hydroxide solution. On filtering, the solution yielded 0.5 g. of a crimson dye and a colorless filtrate, which was acidified and the precipitated phenanthrol recrystallized from benzene; yield 1.2 g.; m. p. 160–161° (cor.); white needles.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.57; H, 5.42.⁷

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An X-Ray Study of the Calcium–Strontium Alloy Series

BY A. J. KING¹

One would be led to predict from the crystal structure, lattice dimensions and position in the periodic table of calcium and strontium that they would be completely miscible in the solid state and hence form a continuous series of solid solutions. Both crystallize at room temperature with the face-centered cubic type of lattice. The edges of the unit cubes are, respectively: Ca, $a_0 = 5.560 \pm 0.006^2$; Sr, $a_0 = 6.076^3$.

To test this, a series of alloys was prepared and an X-ray diffraction analysis made of each to determine the variation of the unit cell dimensions with the composition. According to Vegard⁴ complete miscibility would be indicated by a linear relation between the atomic composition and the lattice dimensions.

The alloys were prepared from resublimed calcium and strontium whose purity was shown by

- (1) Syracuse University, Syracuse, N. Y.
- (2) Hull, *Phys. Rev.*, **17**, 42 (1921).
- (3) Simon and Vohsen, *Z. physik. Chem.*, **133**, 165 (1928); King, *Proc. Natl. Acad. Sci.*, **15**, 337 (1929); Ebert and Hartmann, *Z. anorg. allgem. Chem.*, **179**, 418 (1929).
- (4) L. Vegard, *Z. Physik*, **5**, 17 (1921); E. R. Jette, *Trans. Am. Inst. Mining Met. Eng.*, **111**, 75 (1934).

analysis to be at least 99.0%. The metals were melted in small iron crucibles 0.75 inch in diameter and 2.25 inches high, which were turned from a low carbon steel rod. Tests have shown that very little iron is dissolved by either of these metals in the liquid state if the duration of contact is kept at a minimum. The crucibles containing the alloys were heated in a Pyrex glass tube in an atmosphere of argon by means of a high frequency furnace. Thorough mixing was assured by use of a pure iron wire stirrer which was oscillated with a solenoid at the top of the tube. After cooling the iron crucible was removed from the alloy by turning it off on a lathe. During this process the alloy was bathed in a stream of dry oil to protect it from the action of the atmosphere. The samples for analysis were prepared by rolling the alloys, under oil, into thin sheets from which were cut narrow strips for the X-ray examination.

All alloys of the series crystallized with a face-centered cubic type of lattice.

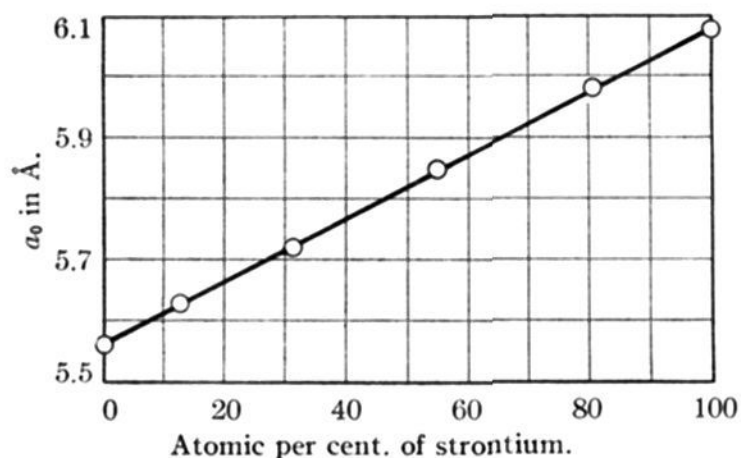


Fig. 1.

The results of the X-ray analysis are summarized in the table and shown graphically in the figure.

At. % Sr	0	10.26	31.37	54.60	80.60	100
a_0 in Å.	5.560	5.627	5.720	5.847	5.980	6.076
Density	1.539	1.666	1.939	2.180	2.416	2.578

It is obvious that the values of a_0 vary directly with the strontium content. Although no thermal analysis has been reported for this system, it is quite apparent from the above results that calcium and strontium form a continuous series of solid solutions at room temperature.

Acknowledgment.—The author wishes to acknowledge the kindness of Prof. G. L. Clark of the University of Illinois, in whose laboratory the preliminary study of this problem was conducted.

RECEIVED MARCH 6, 1942

Dimorphism of Amylcaine Hydrochloride

BY HENRY R. KREIDER AND AMEL R. MENOTTI

During the investigation¹ of the chemical and physical properties of amylocaine hydrochloride (mono-*n*-amylaminoethyl-*p*-aminobenzoate hydrochloride), a local anesthetic used for dental and medical purposes,² two crystalline forms (rectangular plates, melting at 153.5°, and rods, melting at 176°) were obtained. The absence of alcohol of crystallization and water of hydration was demonstrated by a negative Zeisel ethoxyl determination and by the fact that no loss in weight was observed when the crystals were heated above the melting point, although the lower melting form was transformed into the higher melting form under these conditions. Therefore, a dimorphic habit was indicated.

Experimental

Rectangular Plate Form (Fig. 1).—Two grams of commercially available amylocaine hydrochloride was dissolved in 25 cc. of hot water, the solution cooled to room temperature and the resultant crystals were filtered, washed with cold ethanol and dried in vacuum over sulfuric acid; melting point 153.5° (cor.). When kept at the melting point, the liquid solidified spontaneously or upon scratching the microscope slide, yielding the higher melting form. *Anal.* Calcd. for $C_{14}H_{22}O_2N_2 \cdot HCl$: N, 9.77; Cl, 12.36. Found: N, 9.5; Cl, 12.4.

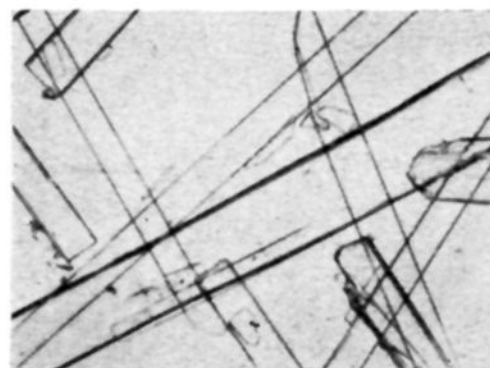


Fig. 1.—Amylocaine hydrochloride, rectangular plate form, m. p. 153.5° ($\times 100$).

Between crossed nicols the crystals appeared as elongated plates with a relatively high birefringence. They exhibited positive elongation and parallel extinction. In convergent polarized light biaxial figures were common, with the acute bisectrix and occasionally an optic axis in the field of view. *Refractive indices* (determined by immersion in organic liquids): $\alpha = 1.510$; $\beta = 1.582$; $\gamma > 1.655$ (all ± 0.002).

Rod Form (Fig. 2).—A saturated solution of amylocaine hydrochloride in boiling *n*-amyl alcohol was cooled slowly in a water-bath to 80°. Long, thick, hexagonal rods were

(1) *J. Am. Med. Assoc.*, **116**, 2020 (1941).

(2) S. D. Goldberg and W. F. Whitmore. *THIS JOURNAL*, **59**, 2280 (1937).

obtained; m. p. 176°. *Anal.* Calcd. for $C_{14}H_{25}O_2N_2 \cdot HCl$: N, 9.77; Cl, 12.36. Found: N, 9.9; Cl, 12.4.

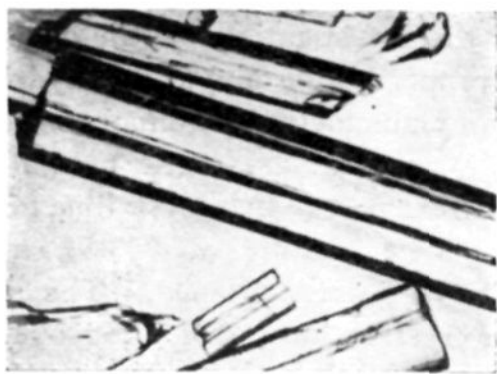


Fig. 2.—Amylcaine hydrochloride, hexagonal rod form, m. p. 176° ($\times 100$).

Between crossed nicols the crystals appeared as long rods with hexagonal cross section exhibiting negative elongation, sharp, parallel extinction and relatively low birefringence. In convergent polarized light partial uniaxial figures were observed, indicating particles with faces parallel to the optic axis. When the crystals were crushed, irregular angular fragments were obtained. An occasional particle did not extinguish sharply when the stage was revolved and in convergent polarized light exhibited a partial uniaxial figure. The optical character was negative. *Refractive indices:* $\omega = 1.582$; $\epsilon = 1.573$ (± 0.002).

Pseudomorphic Habit (Fig. 3).—When the lower melting form was kept at temperatures just below the melting point, the crystals became opaque and showed no tendency to melt at the lower temperature but melted sharply at 176°. This transformation could be followed readily by the change to a lower birefringence during the heating.

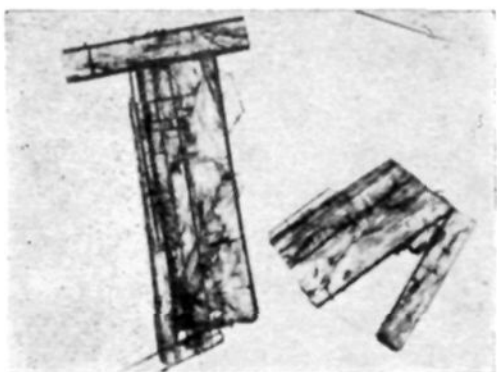


Fig. 3.—Amylcaine hydrochloride, pseudomorphic habit, m. p. 176° ($\times 100$).

CHEMICAL LABORATORY RECEIVED FEBRUARY 14, 1942
OF THE AMERICAN MEDICAL
ASSOCIATION, CHICAGO, ILL.

Sterols. CXLI. 3(α),11,12-Trihydroxycholanolic Acid¹

BY RUSSELL E. MARKER, ANTHONY C. SHABICA, ELDON M. JONES, HARRY M. CROOKS, JR., AND EMERSON L. WITTEBECKER

We have repeated the work of Longwell and Wintersteiner² who attempted to prepare 3(α),11-

dihydroxycholanolic acid by the elimination of the keto group of 3(α),11-dihydroxy-12-ketocholanolic acid by the treatment with hydrazine hydrate and sodium ethylate at 200°. They obtained a compound having presumably two oxygen atoms less than the starting material.

We have obtained from this reaction a compound melting with decomposition at 136° with the empirical formula $C_{24}H_{40}O_5$ (II). The reduction of 3(α),11-dihydroxy-12-ketocholanolic acid (I) to 3(α),11,12-trihydroxycholanolic acid (II) is shown by the analysis and relative ease of its oxidation with chromic anhydride and subsequent Clemmensen reduction to neo-lithobilianic acid (III). Similarly neo-lithobilianic acid was obtained by the action of sodium ethylate and hydrazine hydrate on 11-hydroxy-12-ketocholanolic acid, followed by oxidation of the resulting dihydroxy compound. Reduction to the dihydroxy compound was the major product of both hydrazine reactions.

In addition we have oxidized directly 11-hydroxy-12-ketocholanolic acid to neo-lithobilianic acid. This product was not reported by Barnett and Reichstein³ who oxidized the methyl ester of 11-hydroxy-12-ketocholanolic acid under very mild conditions and obtained 11,12-diketocholanolic acid.

The reduction of a carbonyl to a carbinol group with hydrazine and alkoxide is not without analogy in the literature, for Marker and Lawson⁴ succeeded exclusively in converting pregnan-20(α)-ol-3-one to pregnanediol-3(α),20(α) by the Wolff-Kishner method. Later Dutcher and Wintersteiner⁵ in their investigation of this method of reduction of steroidal ketones showed in several cases that the conversion to a carbinol would take place in preference to the complete reduction to a methylene group.

We thank Parke, Davis and Company for their assistance.

Experimental Part

11,12-Dihydroxycholanolic Acid.—A mixture of 1 g. of 11-hydroxy-12-ketocholanolic acid, 5 cc. of 85% hydrazine hydrate, and 1.8 g. of sodium in 60 cc. of absolute ethanol was heated in a sealed tube for twelve hours at 200°. The product was diluted with water and extracted with ether. The aqueous layer was acidified and extracted with ether. The ether extract was washed with water, dried and evaporated. The product was crystallized from ether-

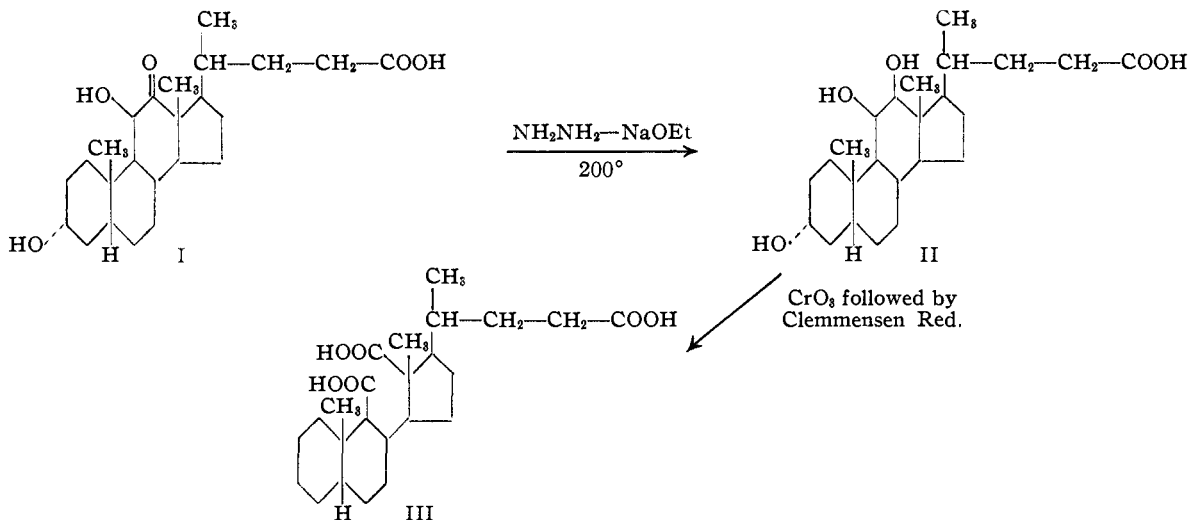
(3) Barnett and Reichstein, *Helv. Chim. Acta*, **XXI**, 926 (1938).

(4) Marker and Lawson, *THIS JOURNAL*, **61**, 852 (1939).

(5) Dutcher and Wintersteiner, *ibid.*, **61**, 1992 (1939).

(1) Original manuscript received June 27, 1941.

(2) Longwell and Wintersteiner, *THIS JOURNAL*, **62**, 200 (1940).



pentane and then from ethyl acetate; m. p. 204–208°; yield, 700 mg.

Anal. Calcd. for $\text{C}_{24}\text{H}_{40}\text{O}_4$: C, 73.4; H, 10.3. Found: C, 73.4; H, 10.4.

This compound was saturated as evidenced by the facts that it did not take up bromine and was recovered unchanged upon attempted hydrogenation with Adams catalyst in acetic acid.

neo-Lithobilianic Acid.—To a solution of 500 mg. of 11,12-dihydroxycholanic acid in 25 cc. of acetic acid was added a solution of 500 mg. of chromic anhydride in 15 cc. of 65% acetic acid. This mixture was allowed to stand at room temperature for one hour. The excess chromic anhydride was destroyed by adding zinc dust. The mixture was filtered and the filtrate was evaporated *in vacuo*. The residue was taken up in ether, washed with water, dried and the solvent was removed. The residue was crystallized from ether; m. p. 257–259°.

Anal. Calcd. for $\text{C}_{24}\text{H}_{38}\text{O}_6$: C, 68.2; H, 9.1. Found: C, 68.4; H, 9.1.

In a similar manner 11-hydroxy-12-ketocholanic acid was oxidized to give a 25% yield of *neo-lithobilianic acid*; m. p. and mixed m. p. with the above acid, 257°.

Anal. Calcd. for $\text{C}_{24}\text{H}_{38}\text{O}_6$: C, 68.2; H, 9.1. Found: C, 68.4; H, 9.2.

3(α),11,12-Trihydroxycholanic Acid.—A mixture of 2.5 g. of 3(α),11-dihydroxy-12-ketocholanic acid, 10 cc. of 85% hydrazine hydrate and a solution of 3.5 g. of sodium in 70 cc. of absolute ethanol was heated in a sealed tube for eight hours at 200°. The reaction mixture was worked up as described for 11,12-dihydroxycholanic acid. The product was crystallized from ether-pentane; m. p. 136° (bubbles); wt., 686 mg. It was also crystallized from ethyl acetate. This compound did not react with bromine and was recovered unchanged upon attempted catalytic reduction.

Anal. Calcd. for $\text{C}_{24}\text{H}_{40}\text{O}_6$: C, 70.5; H, 9.9. Found: C, 70.3; H, 9.8.

Oxidation of 3(α),11,12-Trihydroxycholanic Acid.—To a solution of 0.4 g. of 3(α),11,12-trihydroxycholanic acid in 40 cc. of acetic acid was added a solution of 0.4 g. of

chromic anhydride in 15 cc. of 65% acetic acid. This was allowed to stand at room temperature for one hour. Water was added to the mixture, and the precipitated solid was extracted with ether. The ether layer was washed with water and evaporated. A Clemmensen reduction was run on the residue by refluxing it with 50 cc. of ethanol, 10 g. of amalgamated zinc and adding 60 cc. of concentrated hydrochloric acid over a period of four hours. The zinc was filtered, and water was added to the filtrate. The product was extracted with ether and the ether layer was washed with water and evaporated. The residue was hydrolyzed with alcoholic potassium hydroxide. The free acid was crystallized from ether-pentane; m. p. and mixed m. p. with the *neo-lithobilianic acid* previously prepared, 256–259°.

Anal. Calcd. for $\text{C}_{24}\text{H}_{38}\text{O}_6$: C, 68.2; H, 9.1. Found: C, 68.0; H, 9.0.

SCHOOL OF CHEMISTRY AND PHYSICS

PENNSYLVANIA STATE COLLEGE

STATE COLLEGE, PENNA.

RECEIVED JANUARY 21, 1942

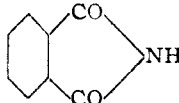
Non-peroxide Catalysts for the Reaction between Sulfur Dioxide and Olefins¹

BY C. S. MARVEL, L. F. AUDRIETH AND W. H. SHARKEY

A tertiary amine oxide, R_3NO , may be considered as a nitrogen analog of a peroxide and this has led us to try representatives of this group of compounds as catalysts for the addition of sulfur dioxide to an olefin or an acetylene to produce polymeric sulfones.

Trimethylamine oxide and dimethylaniline oxide proved to be catalysts for the reaction with such representative compounds as 1-pentene, 1-hexene, 1-heptene, 2-butene and 1-pentyne. The

(1) This is the thirteenth communication on the reaction between sulfur dioxide and olefins. For the twelfth see *THIS JOURNAL*, **61**, 2714 (1939).

POLYSULFONES FROM VARIOUS CATALYSTS					
Unsatd. compound	Amount, cc.	Catalyst to be tested	Amount in grams	Time, hr.	Yield of polysulfone, g.
1-Pentene	5	NH ₂ OH·HCl	0.5	12	1.13
1-Pentene	5	(CH ₃) ₃ NO	.5	12	4.5
1-Pentene	5		.5	12	3.5
1-Pentene	5	(CH ₃) ₃ NO	.2	18	3.09
1-Pentene	5	(CH ₃) ₃ NO	.2		
		HCl	2 cc., sp. gr. 1.19	18	5.17
1-Pentene	5	C ₆ H ₅ (CH ₃) ₂ NO	5 cc., soln. in concd. HCl	12	1.0
1-Hexene	5	(CH ₃) ₃ NO	0.2	12	6.15
		HCl	2 cc. dil.		
1-Heptene	5	(CH ₃) ₃ NO	0.2	12	5.04
		HCl	2 cc., sp. gr. 1.19		
1-Pentyne	10	(CH ₃) ₃ NO	0.5	18	13.38
2-Butene	10	(CH ₃) ₃ NO	.5	18	16.00
2-Pentene	10	(CH ₃) ₃ NO	.5	18	2.69
1-Heptene	5	(CH ₃) ₄ NCl	.2	16	5.38
1-Pentene	5	(CH ₃) ₄ NCl	.2	12	3.25
1-Pentene	5	(C ₂ H ₅) ₄ NBr	.2	60	4.42
1-Pentene	5	(<i>n</i> -C ₇ H ₁₅)(<i>n</i> -C ₄ H ₉) ₂ NI	.1	60	None
1-Heptene	5	(<i>n</i> -C ₇ H ₁₅)(<i>n</i> -C ₄ H ₉) ₂ NI	.1	16	None

addition of halogen acid² to give the salt of the amine oxide increased the catalytic activity to a marked extent. Even hydroxylamine hydrochloride proved to have some activity as a catalyst for the reaction. More surprising was the fact that both tetramethylammonium chloride and tetraethylammonium bromide were catalysts for the reaction. Their activity, however, was not great. Tests with some quaternary ammonium iodides showed these were not catalysts for the addition reaction. Phthalimide also showed some catalytic activity.

Experimental

Trimethylamine oxide and dimethylaniline oxide were made by the method described by Hickinbottom.³

The polymerization reactions were carried out in pressure bottles. The unsaturated compounds and sulfur dioxide with a little ethyl alcohol were placed in the bottle with the substance to be tested as a catalyst. The sealed reaction mixture was allowed to stand for the specified time, then opened, the excess sulfur dioxide allowed to evaporate and the product isolated by the usual procedure. The results are summarized in the following table.

Trimethylamine oxide did not catalyze the addition of sulfur dioxide to vinyl chloride. Hydrazine, phenylhydrazine, cupferron, phenylglyoxal oxime, azoxybenzene, nitrobenzene, semicarbazide hydrochloride, dimethyl

formamide, and hydrazocarbamide showed no catalytic activity at ordinary temperatures.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

RECEIVED JANUARY 26, 1942

Association Effects in the Raman Spectra of Solutions of Thiophenol in Donor Solvents

BY ROBERT H. SAUNDERS, M. J. MURRAY AND
FORREST F. CLEVELAND

While the O-H stretching vibration gives strong absorption in the infrared and is quite suitable for use in the study of hydrogen bonding, the O-H frequencies in Raman spectra produce broad bands, so diffuse that in a great number of cases they are not even observed. On the other hand, the Raman spectra of mercaptans show a strong S-H line at 2570 cm.⁻¹ which is in a region not occupied by other fundamentals. For this reason it was hoped that a hydrogen bond study could be made of solutions of thiophenol such as Gordy and Stanford¹ had done in the infrared. Consequently, Raman spectra were obtained for pure thiophenol and for its solutions in benzene, dioxane, diisopropyl ether, pyridine, dibenzylamine and diisobutyl ketone. All compounds used were of good quality and were distilled before mixing. The apparatus and experimental technique used in obtaining the spectra are discussed

(2) Kharasch and Sternfeld [THIS JOURNAL, **62**, 2559 (1940)] have shown that the addition of hydrochloric acid increases the activity of the peroxide, ascaridole, as a catalyst for polysulfone formation.

(3) Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Company, New York, N. Y., 1938, p. 277.

(1) Gordy and Stanford, THIS JOURNAL, **62**, 497 (1940).

elsewhere.² Hg 4358 Å. was used for excitation, and the slit width of the spectrograph was 0.08 mm.

In order to determine whether mixing had altered disproportionately the intensity of the S-H line, the strength of the 2570 line was compared with that of the 700 cm^{-1} line of thiophenol on the same spectrogram. This latter line was chosen as a comparison line because it is neither too weak nor too strong for accurate intensity measurement, because it does not coincide with any lines of the various solvents employed, and because comparison of the intensity ratio of this line to lines other than 2570 cm^{-1} indicated no noticeable effect due to association. Semi-quantitative comparison was attained by use of a set of standard lines of regularly varied intensity.³

The results are listed in Table I. The number in parentheses following the Raman frequency represents intensity. The 700 cm^{-1} line which was used as a standard is arbitrarily given the value of 4 on each spectrogram. No attempt was made to compare the different spectrograms with each other. In general, the solutions employed were more dilute than those used by Gordy and Stanford. This was for the purpose of giving the mercaptan molecules as much chance to form hydrogen bonds as was experimentally feasible, since preliminary experiments indicated that the 50% by volume solutions did not show so large an effect as had been anticipated from the infrared data.

TABLE I
THE EFFECT OF DONOR SOLVENTS UPON THE S-H FREQUENCY OF THIOPHENOL

Solvent	Hours of exposure	Volume, % of thiophenol	S-H frequency	
			Raman cm^{-1} I	Infrared ¹ cm^{-1}
Thiophenol (pure)	1	100	2569(7)	2577
Benzene	4	25	2571(7)	2577 ^a
Diisobutyl ketone	4 and 11	25	2570(6)	..
Diisopropyl ether	4	25	2570(5)	2557 ^b
Pyridine	4	50	2569(6)	2463 ^b
Pyridine	4 and 9	25	2571(3)	2463 ^b
Dioxane	4 and 8	25	2569(3)	..
			2536(2)	
Dibenzylamine	1	25	2571(6) ^c	2475 ^b

^a Dilute solution. ^b Fifty % by volume solution. ^c Solid separated from this solution at the end of one hour. Intensity reading somewhat in doubt.

As in the infrared work of Gordy and Stan-

(2) Cleveland, Murray, Haney and Shackelford, *J. Chem. Phys.*, **8**, 153 (1940); Cleveland, Murray, Coley and Komarewsky, *ibid.*, **10**, 18 (1942).

(3) Cleveland and Murray, *ibid.*, **7**, 396 (1939).

ford,¹ benzene was found to have negligible effect on the S-H frequency in the thiophenol-benzene solution. For mixtures of the mercaptan in diisobutyl ketone and diisopropyl ether the Raman line for the S-H stretching vibration is unchanged in frequency, somewhat broadened and only slightly decreased in intensity. For thiophenol-pyridine solutions the results are at complete variance with the infrared findings. In neither the 50% nor the 25% solutions is there Raman spectra evidence for an altered frequency. Furthermore, although in the 25% solution there is considerable decrease in the strength of the S-H line, it is evident that even in this more dilute solution the S-H groups of a sizable proportion of the thiophenol molecules are little affected by the presence of pyridine. The infrared results showed not only a shift of 114 cm^{-1} but also a large increase in absorptive power as compared to the pure mercaptan. The infrared showed no evidence for a band due to the unmodified S-H frequency in pyridine solution, but this may in part be caused by lack of resolution.

The Raman spectra results for the solution of thiophenol in dioxane are most striking. In this case the S-H frequency appears as a doublet composed of the original, unshifted, slightly broadened line and a new line (not observed in the spectra of either of the pure compounds) at 2536 cm^{-1} which is somewhat weaker and broad but clearly resolved from the 2569 cm^{-1} line. This is the only one of the compounds studied for which there is Raman spectra evidence of a modified frequency. In all the other cases tested in this investigation, if modified frequencies result they must be very weak or so broad and diffuse that they failed to register on the photographic emulsion in the time allotted.

DEPARTMENTS OF CHEMISTRY AND PHYSICS
ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO, ILLINOIS RECEIVED OCTOBER 24, 1941

Boiling Point-Composition Data of the Methyl Alcohol-Dioxane System

BY FRANK L. PADGITT,¹ EDWARD S. AMIS AND DAVID W. HUGHES²

In order to further extend the data of the methyl alcohol-dioxane system given by Amis,

(1) Now employed by Ethyl Gasoline Corporation, Baton Rouge, La.

(2) Now employed by Tennessee Coal, Iron and Railway Company, Birmingham, Alabama.

Choppin and Padgitt³ the boiling point-composition curve has been determined.

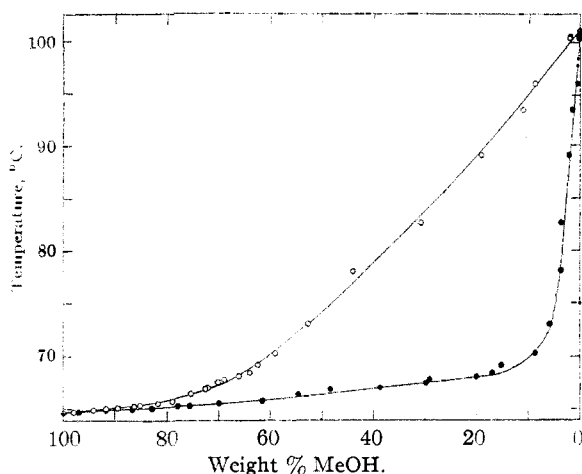


Fig. 1.—Vapor phase, O; liquid phase, ●.

The methyl alcohol and dioxane were purified as previously described³; the apparatus used was that of Othmer.⁴ Equilibrium between the vapor and liquid phases was established after

TABLE I
BOILING POINT-COMPOSITION DATA FOR THE METHYL
ALCOHOL-DIOXANE SYSTEM AT ONE ATMOSPHERE

B. p., °C.	Wt., % liquid	MeOH vapor
64.60	100	100
64.72	96.5	98.1
64.90	91.9	94.2
64.96	86.7	91.9
65.10	82.9	89.4
65.27	78.0	86.3
65.34	75.7	85.2
65.55	69.7	81.7
65.78	61.7	77.9
66.50	54.6	75.7
66.94	48.4	72.6
67.10	38.8	72.2
67.60	29.8	70.2
67.89	29.0	67.9
68.20	20.0	66.1
68.50	17.0	63.9
69.30	15.4	62.5
70.40	9.7	59.0
73.20	6.0	52.7
78.20	3.9	44.1
82.80	3.7	30.8
89.20	2.4	19.1
93.50	1.6	11.1
96.04	0.7	8.7
100.38	.3	1.9
100.54	.3	1.8
101.05	.0	0.0

(3) Amis, Choppin and Padgitt, *THIS JOURNAL*, **64**, 1207 (1942).

(4) Othmer, *Ind. Eng. Chem.*, **20**, 743 (1928).

about three hours for each determination. Temperatures were measured with calibrated thermometers graduated in 0.05° with a precision of $\pm 0.05^\circ$. The liquid and vapor phases were analyzed by means of refractive index using the values reported by Amis, Choppin and Padgitt.³ The results are tabulated in the table and represented graphically in the figure.

CONTRIBUTION FROM THE
CHARLES EDWARD COATES CHEMICAL LABORATORY
LOUISIANA STATE UNIVERSITY
BATON ROUGE, LA.

RECEIVED JULY 29, 1941

Addition Compounds of Tetrahydrothiopyran

BY HARRY J. WORTH AND HELMUT M. HAENDLER

Two addition compounds of tetrahydrothiopyran (pentamethylene sulfide) and inorganic metal salts have been reported: $\text{HgCl}_2 \cdot (\text{CH}_2)_5\text{S}$ by Grischkewitsch-Trochimowski¹ and $x\text{HgI}_2 \cdot (\text{CH}_2)_5\text{S}$ by Bost and Conn.² This sulfide forms addition compounds with other metal halides, offering comparison with dithiane,³ dioxane,⁴ and morpholine.⁵ Tetrahydrothiopyran exhibited less tendency to form addition compounds than did dithiane or dioxane, but greater tendency than morpholine.

The compounds are crystalline, somewhat sensitive to water, and are white, except for the yellow gold(III) chloride, tin(IV) bromide, and platinum(II) iodide, the red-brown gold(III) bromide, and the orange-red palladium(II) chloride compounds. There was some indication of reaction with silver iodide, silver bromide, and tin(IV) iodide, but no compounds could be isolated. The following compounds gave no results: copper(II) fluoride, cadmium halides, zinc chloride, iron(III) chloride, arsenic(III) iodide, antimony(III) iodide and chloride, germanium(IV) chloride, and silicon(IV) chloride.

The thiopyran was prepared by a modification of the methods of von Braun⁶ and Clarke,⁷ using 100 g. of benzoylpiperidine and 110 g. of phosphorus pentachloride. The benzonitrile was hydrolyzed by warming under reflux, the dichloropentane steam distilled, and converted to tetra-

(1) Grischkewitsch-Trochimowski, *Chem. Zentr.*, **87**, I, 1503 (1923).

(2) Bost and Conn, *Ind. Eng. Chem.*, **23**, 93 (1931).

(3) Bouknight and Smith, *THIS JOURNAL*, **61**, 28 (1939).

(4) Rheinboldt, Luyken and Schmittmann, *J. prakt. Chem.*, **149**, 30 (1937).

(5) Haendler and Smith, *THIS JOURNAL*, **63**, 1164 (1941).

(6) von Braun, *Ber.*, **37**, 2915 (1904).

(7) Clarke, *J. Chem. Soc.*, **101**, 1785 (1912).

TABLE I
 ADDITION COMPOUNDS OF TETRAHYDROTHIOPYRAN

Inorg. salt	Solvent	Solubility	M. p., °C.	Formula	Metal analyses, %	
					Calcd.	Found
HgBr ₂	Alcohol	Sl. sol. hot aq. alc.	101-105	HgBr ₂ ·(CH ₂) ₆ S	43.36	43.26
CuCl ₂	Alcohol	Ins. aq., org. solv.	154.5-157	CuCl·(CH ₂) ₆ S	31.59	31.55
Cu ₂ Cl ₂	Alc. HCl	Same	154.5-160	CuCl·(CH ₂) ₆ S	31.59	31.50
CuBr ₂	Alcohol	Same	123-124	CuBr·(CH ₂) ₆ S	25.88	25.85
Cu ₂ Br ₂	Alc. KBr	Same	121.5-122.5	CuBr·(CH ₂) ₆ S	25.88	25.79
Cu ₂ I ₂	Alc. KI	Same	164-165 d.	CuI·(CH ₂) ₆ S	21.73	21.85
HAuCl ₄	Ether	Sl. sol. alc., ins. eth.	120-122 d.	AuCl ₃ ·(CH ₂) ₆ S	48.60	48.39
HAuCl ₄	Alcohol	Ins. alc. eth.	179-182 d.	AuCl·(CH ₂) ₆ S	58.89	58.66
HAuBr ₄	Ether	Sl. sol. alc. eth.	140-145 d.	AuBr ₃ ·(CH ₂) ₆ S	36.58	36.70
^a	Alcohol	Sl. sol. hot alc.	173-179 d.	AuBr·(CH ₂) ₆ S	51.99	51.83
SnCl ₄	^b	Sol. chl., dec. aq.	149-151.5	SnCl ₄ ·2(CH ₂) ₆ S	25.53	25.57
SnBr ₄	Chlorof.	Sol. chl., dec. aq.	149.5-151	SnBr ₄ ·2(CH ₂) ₆ S	18.36	18.45
H ₂ PtCl ₆ -KI ^c	Alcohol	Ins. alc.	194.5-196 d.	PtI ₂ ·2(CH ₂) ₆ S	29.88	29.98
PdCl ₂	Acetone-H ₂ O	Sl. sol. acet., ins. aq.	146.5-148.5 d.	PdCl ₂ ·2(CH ₂) ₆ S	27.93	28.07

^a AuBr₃·(CH₂)₆S boiled with alcohol and excess thiopyran. ^b Thiopyran and tin(IV) chloride mixed directly. ^c Excess potassium iodide solution added to chloroplatinic acid in alcohol, precipitate dissolved by heating, and thiopyran added till no further precipitation.

hydrothiopyran by refluxing with excess sodium sulfide in ethanol.

The addition compounds were formed by dissolving the metal salt in ethanol or ether, adding salt or acid if necessary, and adding slight excess of sulfide, sometimes dissolved in the solvent. The data on the complexes are given in Table I.

DEPARTMENT OF CHEMISTRY
 UNIVERSITY OF WASHINGTON
 SEATTLE, WASHINGTON RECEIVED FEBRUARY 2, 1942

Structures of Complex Fluorides. Rubidium Hexafluogermanate

BY W. B. VINCENT AND J. L. HOARD

In an earlier paper¹ we have reported the X-ray determination of structure for the isomorphous crystalline compounds potassium hexafluogermanate and ammonium hexafluogermanate, R₂GeF₆. Upon the basis of X-ray data obtained from a single specimen of what we supposed was rubidium fluogermanate, we stated at that time that this substance crystallizes in a more complex structural type than do the corresponding potassium and ammonium salts. This particular specimen occurred as a hexagonal prism, almost needle-like in shape, whereas we have since obtained only hexagonal tablets and plates by recrystallizing rubidium fluogermanate from aqueous solution at room temperature. X-Ray study of a number of these tabular crystals shows that they crystallize in the same structural type as do

(1) J. L. Hoard and W. B. Vincent, *THIS JOURNAL*, **61**, 2849 (1939).

potassium and ammonium fluogermanates. The single needle-like specimen may or may not have been rubidium fluogermanate: the values of the lattice constants indicate that it may have been a different crystalline modification of closely related and only slightly more complicated structure than that to be discussed here. In any case we must correct our earlier statement at least to the extent of asserting that the usual and presumably the stable form at room temperature of rubidium fluogermanate is fully isomorphous with the corresponding ammonium and potassium salts.

The X-ray data for Rb₂GeF₆ lead to a hexagonal unit cell with $a = 5.82$, $c = 4.79$ Å., space-group $D_{3d}^3 - C\bar{3}m$, containing one stoichiometric molecule. The atomic coordinates² are Ge in (a): 000; 2Rb in 2(d): $\frac{1}{3}$ $\frac{2}{3}$ u ; $\frac{2}{3}$ $\frac{1}{3}$ \bar{u} with $u = 0.695$; 6 F in 6(i): xxz , etc., with $x = 0.144$, $z = 0.213$.

The methods used in establishing this structure closely paralleled those previously described.¹ A comparison of calculated with observed reflection amplitudes for over one hundred forms in rubidium fluogermanate led to generally excellent agreement. Having presented¹ the corresponding data in detail for potassium fluogermanate, and ammonium hexafluogermanate, it seems unnecessary to reproduce the rather extensive tables³ for rubidium hexafluogermanate in this note. In addition we find that a Fourier projec-

(2) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder-Borntraeger, Berlin, 1935, Vol. I, p. 258.

(3) The amplitude data for rubidium hexafluogermanate are available in the Thesis of W. B. Vincent, "The Structures of Some Fluosilicates and Fluogermanates," Cornell University Library, 1940.

tion of relative electron density along a using experimental ($0kl$) amplitude data is in satisfactory agreement with the parameter values given above.

Rubidium fluogermanate is an aggregate of K^+ and practically regular octahedral GeF_6^- ions (for diagrams of the structural type see ref. 1). The lattice constants and parameter values are only very slightly different from those found for ammonium fluogermanate, so that corresponding interatomic separations are virtually identical

in the two cases. The near identity in the effective radii of rubidium and ammonium ions appearing in corresponding compounds has been repeatedly observed excepting in cases where ammonium ion is restricted to a small coordination number (usually four) through the formation of strong hydrogen bonds. We may conclude again¹ that hydrogen bonding plays a relatively minor role in ammonium fluogermanate.

DEPARTMENT OF CHEMISTRY
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RECEIVED FEBRUARY 20, 1942

COMMUNICATIONS TO THE EDITOR

ELECTRON MICROSCOPE OBSERVATIONS OF COLLAGEN

Sir:

Electron micrographs have been made of collagen fibers from a variety of sources, including rat tail tendon, beef tendons and ligaments, and human skin. Fibers were obtained either by teasing small bits of tendon in water or by dissolving the material in acetic acid and reprecipitating the fibers by neutralization.

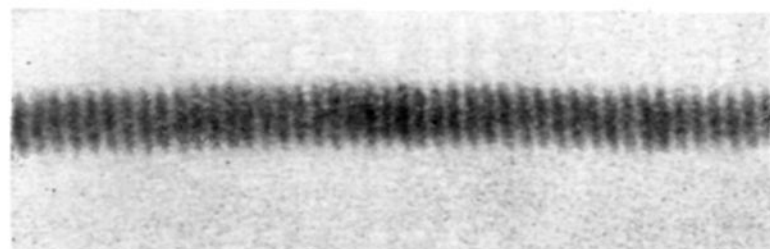


Fig. 1.—Electron micrograph of collagen fibers from beef tendon, magnification 25,000 \times .

Under appropriate conditions the fibers appear characteristically cross-striated, the relatively opaque and transparent bands extending uniformly across the fiber (see Fig. 1). The average distance between like bands can be measured with an accuracy of about 3%. The interband distance is independent of fiber width and varies considerably from one fiber to another; the extremes thus far measured are 902 and 522 \AA ., though the range shown in the fibers of any single preparation is more restricted.

Recent X-ray diffraction investigations in this

Laboratory [R. S. Bear, *THIS JOURNAL*, **64**, 727 (1942)] have demonstrated the presence in collagen of a fiber-axis periodicity of approximately 640 \AA . This spacing was obtained from all the types of collagen mentioned above and appears to be characteristic of this protein in intact tissues. There seems little doubt that the periodicities observed in the electron micrographs represent a manifestation of the X-ray diffraction periodicity in intact tendon and that the phenomenon is a consequence of the structure and arrangement of the collagen molecules in the fibers. The range of spacings observed in the electron micrographs is doubtless due to the special conditions required for the preparation of the material, chief among which are the isolation and vacuum drying of individual fibers. It is reasonable to expect individual fibers to behave differently when isolated than when present in compact bundles as in normal tendon where lateral restraints, possibly by enclosing membranes and cement substance, restrict their behavior mechanically. This interpretation is being tested by an X-ray diffraction study of teased fibers similar to those observed with the electron microscope. In addition, the effect of various physical and chemical conditions on the appearance of the fibers in the electron micrographs is being further investigated in an effort to get more information concerning the molecular architecture of collagen.

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