

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)							
$C_{t+r+vib.}$		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.

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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. Fennicae*, **A41**, No. 5 (1934).

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

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