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			
$P = 0$ (Pitzer and Gwinn)	16.11				16.87		
$C_{t.+r.+vib.}$		15.09	15.37	15.82			
$C_{I.R.}$		1.13	1.08	0.99			
$C_{I.R.}$ (Pitzer and Gwinn)	1.17				0.98		

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 Todd[2] provided evidence that the acetyl group in the acetylretene of Bogert and Hasselstrom[3] occupies the 3-position. It is of interest to note that when this reaction is applied to 9,10-dihydrophenanthrene[4] or 9,10-dihydroretene[5] 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 phenanthrone 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-methylphenanthrene[6] 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-methylphenthrene 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, 6.19[7] (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.

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 $C_{23}H_{17}O_8N_3$: N, 9.07. Found: N, 9.35.[7]

The Oxidation of 3-Acetyl-1-methylphenanthrene (D. T.).—Seventy-five hundreds 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. KING[1]

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 Vegard[4] 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).