TABLE X

ENTROPY OF ETHYLENE AT 1 ATMOSPHERE FROM SPECTROSCOPIC DATA

	$T =$ 169.40°K.	$T =$ 298.10°K.
$S_{\text{trans.}} = 3/2\,R \ln M + 5/2\,R \ln T - R \ln P - 2.300$	33.130	35.938
$S_{\text{rot.}} = R/2 \ln I_1 I_2 I_3 + 3/2\,R \ln T - R \ln \sigma + 267.649$	14.192	15.876
$S_{\text{vib.}} = R \sum\limits_{\nu_1 \text{ to } \nu_{12}} \left[\ln \frac{e^x}{e^x - 1} + \frac{x}{e^x - 1} \right]$	0.031	0.656
where $x = hc\nu/kT$		
Total entropy in cal./deg. per mole	47.35	52.47

TABLE XI

COMPARISON OF EXPERIMENTAL AND SPECTROSCOPIC VALUES OF THE ENTROPY OF ETHYLENE

		$T =$ 169.40°K.	$T =$ 298.10°K.
		Cal./deg. per mole	
	Absolute	52.86	57.98
Spectroscopic	Less nuclear spin entropy	47.35	52.47
Experimental	Actual gas	47.21 ± 0.1	...
	Ideal gas	47.36	52.48

The excellent agreement between the spectroscopic and experimental values of the entropy of ethylene indicates it is correct to use the third law value in thermodynamic calculations. It also gives more experimental substantiation to the conclusion of Kemp and Pitzer that no molecules other than hydrogen and deuterium will retain any entropy due to the persistence of rotation in the crystal below 10°K.

Summary

The heat capacity of ethylene has been measured from 15°K. to the boiling point. Evidence has been presented to indicate that the sharp rise in the heat capacity curve immediately below the melting point is the true course of the curve and is not due to premelting.

The melting point was found to be 103.95 ± 0.05°K., the boiling point 169.40 ± 0.05°K., (0°C. = 273.10°K.), the heat of fusion 800.8 ± 0.8 cal./mole, the heat of vaporization 3237 ± 3 cal./mole.

The vapor pressure of ethylene has been measured and the results have been represented by the equation

liquid ethylene, 123 to 170°K., (0°C. = 273.10°K.)

$$\log_{10} P_{(\text{Int. cm.})} = -(962.794/T) + 9.80431 - 0.0184522\,T + 0.000030870\,T^2$$

The entropy of ethylene (ideal gas) at 1 atmosphere and at the boiling point 169.40°K. has been calculated from the calorimetric data to be 47.36 cal./deg. per mole and compared with the value 47.35 obtained from spectroscopic data. These values of the entropy are the ones ordinarily used in thermodynamic calculations and do not contain the nuclear spin contribution of R ln 2 for each hydrogen atom. The close agreement of the experimental and spectroscopic values of the entropy substantiates the conclusion that no molecules, other than hydrogen and deuterium, containing symmetrically placed hydrogens will have any residual entropy due to the persistence of rotation of the molecules in the crystal below 10°K.

BERKELEY, CALIF. RECEIVED MAY 3, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Synthesis of 1,4-Dimethylphenanthrene by the Pschorr Reaction, and the Non-identity of the Product with the 1,4-Dimethylphenanthrene of Bardhan and Sengupta[1]

BY RUSSELL BLISS AKIN,[2] GELU S. STAMATOFF AND MARSTON TAYLOR BOGERT

In a recent article, Bogert and Stamatoff[3] described the synthesis of 1,3-dimethylphenanthrene by the Pschorr process and recorded the properties of their product.

After this research had been completed and the results submitted for publication, but before the article appeared, Bardhan and Sengupta[4] reported the preparation of 1,4-dimethylphenanthrene by the cyclodehydration (with phosphorus pentoxide) of ethyl 2-(beta-2′,5′-dimethylphenylethyl)-cyclohexanol-2-carboxylate (X) to the corresponding octahydrophenanthrene derivative (XI), and fusion of the latter with selenium.

Upon comparing with the Bogert and Stamatoff products the constants given by Bardhan

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[1] Presented before the Division of Organic Chemistry, at the Chapel Hill Meeting of the American Chemical Society, April 13, 1937.

[2] Ferguson Fellow, Columbia University, 1934–1935 and 1936–1937.

[3] Bogert and Stamatoff, *Rec. trav. chim.*, **52**, 583 (1933).

[4] Bardhan and Sengupta, *J. Chem. Soc.*, 2520–2526 (1932).

and Sengupta for their dimethylphenanthrene and its picrate, we were struck immediately by the fact that the melting points of the two sets were practically the same. It seemed important, therefore, to find out whether the two hydrocarbons were identical or not.

Both syntheses began with what were believed to be the pure xylenes, the Calcutta investigators using the *p*- and we the *m*-isomer, and the first few steps in the two cases, up to and including the preparation of the dimethylbenzyl cyanide (IV), were similar. From that point, our synthesis followed the customary Pschorr procedure, to the 1,3-dimethylphenanthrene-10-carboxylic acid, from which the carbon dioxide was then driven off. The route followed by Bardhan and Sengupta, on the other hand, led them to their goal by the steps already mentioned.

A logical line of attack upon the problem seemed to us to be the synthesis of 1,4-dimethylphenanthrene by some other method, preferably one not likely to lead to any molecular rearrangements, and for this we chose the familiar Pschorr method.

The result was not unexpected, for the 1,4-dimethylphenanthrene obtained in this way was quite different from the Bardhan and Sengupta product.

Two possible explanations of this discrepancy suggested themselves. At first we thought that perhaps the Indian investigators had used as initial material a xylene which, although labeled "Para Xylene," actually contained considerable amounts of the *m*-isomer. This doubt, however, could not be resolved satisfactorily, because they did not describe any crystalline solids of definite melting point, and the only comparison possible, therefore, was with the boiling points of liquids under reduced pressure, where no pronounced difference between the *m*- and *p*-isomers could be expected.

There remained, then, the possibility of a molecular rearrangement, resulting in the migration of the methyl group from position 4 to 3. Inasmuch as our experiments have shown that the pure 1,4-dimethylphenanthrene is not rearranged to the 1,3-isomer by fusion with selenium, under the conditions employed by Bardhan and Sengupta, it follows that this change must have occurred prior to the formation of the hydrocarbon, perhaps during the initial breakdown of the octahydro ester (XI) in the long continued high temperature fusion with selenium.

In the important field of polycyclic hydrocarbons, notably the phenanthrenes and cyclopentenophenanthrenes, both natural and synthetic products frequently contain hydroaromatic rings, the determination of whose constitution commonly includes a dehydrogenation by fusion with sulfur or selenium.

It has generally been taken for granted that this dehydrogenation does not disturb alkyl groups directly attached to the cycles unless that union is a quaternary one, in which case the alkyl is entirely eliminated.

If, therefore, it can be shown that high temperature fusion with sulfur or selenium may cause a migration of alkyl groups in non-quaternary union with the cycle, any deduction as to the constitution of the original compound, based upon the nature of the dehydrogenation product, may prove to be quite erroneous.

Haworth, Mavin and Sheldrick[5] pointed this out some three years ago, when they reported that in attempting to obtain 1,5-dimethylphenanthrene by dehydrogenation of either 4,8-dimethyl-1,2,3,4-tetrahydrophenanthrene, or of the ester corresponding to the Bardhan and Sengupta compound (XI) with the two methyl groups in positions 1 and 5, the main product in both cases was the 1,8-dimethyl derivative, with but little of the desired 1,5-isomer. In the case of another isomer of (XI), whose methyl groups were at 3 and 5, instead of 1 and 5, the result was again abnormal, and there was isolated only the 1,6-dimethyl derivative and none of the 3,5-isomer. They found also that the dehydrogenation of 4-methyl-1,2,3,4-tetrahydrophenanthrene yielded neither 4- nor 1-methylphenanthrene. An attempt to synthesize the 2,4-dimethyl isomer by the Bardhan and Sengupta process, likewise failed to give the compound expected. Haworth and his co-workers called attention to the fact that, in the experiments conducted by them, there was involved a migration of a methyl group from position 4 to 1, and suggested an explanation. In the experiments recorded in the present communication, however, the shift which occurs is not to the *p*-, but to the adjacent C.

The work of Ruzicka and his associates,[6] on the selenium dehydrogenation of sterols and

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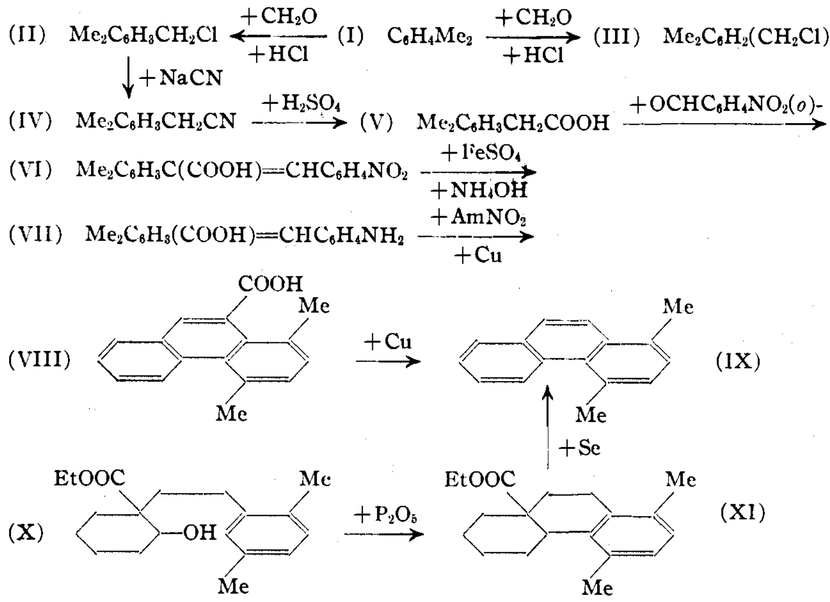
[5] Haworth, Mavin and Sheldrick, *J. Chem. Soc.*, 454 (1934).

[6] (a) Ruzicka and Thomann, *Helv. Chim. Acta*, **16**, 216 (1933); (b) Ruzicka, Goldberg and Thomann, *ibid.*, **16**, 812 (1933); (c) Ruzicka, Thomann, Brandenberger, Furter and Goldberg, *ibid.*, **17**, 200 (1934).

Flow Sheet



(II) $Me_2C_6H_3CH_2Cl \xleftarrow[+HCl]{+CH_2O}$ (I) $C_6H_4Me_2 \xrightarrow[+HCl]{+CH_2O}$ (III) $Me_2C_6H_2(CH_2Cl)_2$

$\downarrow +NaCN$

(IV) $Me_2C_6H_3CH_2CN \xrightarrow{+H_2SO_4}$ (V) $Me_2C_6H_3CH_2COOH \xrightarrow{+OCHC_6H_4NO_2(o)\text{-}}$

(VI) $Me_2C_6H_3C(COOH){=}CHC_6H_4NO_2 \xrightarrow[+NH_4OH]{+FeSO_4}$

(VII) $Me_2C_6H_3(COOH){=}CHC_6H_4NH_2 \xrightarrow[+Cu]{+AmNO_2}$

Tabulation of Constants

A = 1,3-Series of Bogert and Stamatoff,[3] and/or of Akin, Stamatoff and Bogert.
B = 1,3-Series of Haworth, Mavin and Sheldrick.[5]
C = 1,4-Series of Bardhan and Sengupta.[4]
D = 1,4-Series of Akin, Stamatoff and Bogert.

Roman numerals refer to Flow Sheet. All melting points are corrected.

Compound	A	B	C	D
II, b. p.	86–87 at 7 mm.		85–86 at 7 mm.	86–87 at 7 mm.
	116–118 at 16 mm.			100.5–101.5 at 15 mm.
III, m. p.	94.5–95.5			132
IV, b. p.	115–117 at 6 mm.			m. p. 28
	140 at 11 mm.		115–119 at 6 mm.	116–118 at 6 mm.
				142–143 at 19 mm.
V, m. p.	104			129.5
Ethyl ester of V, b. p.	113–115 at 4 mm.		114 at 4 mm.	114–116 at 4 mm.
VI, m. p.	187–188			173.5–174
VII, m. p.	217.5–218.5			199–200.5
VIII, m. p.	188–189			202–203
IX, m. p.	76–77	75–76	77	50–51
IX, picrate, m. p.	153–155	154–155	155	147–148
IX, styphnate, m. p.		165–166		135.5–136.5
IX, quinone, m. p.	218–219	215–216		212–214
IX, quinoxaline, m. p.		154–155		

related substances, has shown to what an extent the nature of the product is influenced by such factors as temperature, duration of heating, etc.

The Flow Sheet shows the steps in our synthesis of both 1,3- and 1,4-dimethylphenanthrenes, and the final steps in the Bardhan and Sengupta synthesis of the 1,4-isomer.

The Tabulation of Constants, which follows it, presents the data upon which we base our belief that the Bardhan and Sengupta product is the 1,3-isomer, and that the compound described by us as the 1,4-isomer is a different hydrocarbon.

Acknowledgments.—This investigation was made possible by the generous action of the Trustees of the Ella Sachs Plotz Foundation in contributing funds for its support. For that welcome assistance, we are deeply grateful.

Experimental

***p*-Xylene.**—Because of the high cost of the pure article, many investigators find it necessary to make their own *p*-xylene, by preparing first the *p*-methyl benzylchloride from toluene, paraformaldehyde and hydrochloric acid,[7] and

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(7) (a) Stephen, Short and Gladding, *J. Chem. Soc.*, **117**, 510 (1920); (b) Blanc, *Bull. soc. chim.*, [4] **33**, 313 (1923).

then reducing this chloride.[8] In our own experiments, we found the Gladstone–Tribe copper–zinc couple very satisfactory for this reduction; yield 73%.

Unfortunately, the xylene obtained by this synthesis is a mixture of the *p*- and *o*-isomers. Oxidized to the corresponding phthalic acids by potassium permanganate, this mixture was found to contain 26–32% of the *o*-xylene. Subjected to the Clarke and Taylor[9] process of purification, the crude *p*-xylene gave yields of about 60% of the pure hydrocarbon, melting at 14–15°, in agreement with the literature.

The Chloromethylation of *m*- and *p*-Xylene.—After considerable experimentation with the various modifications of this reaction already in the literature, the following improved procedure was worked out for the mono- and dichloromethylation of both *m*- and *p*-xylene.

A mixture of the xylene with an equal volume of concentrated hydrochloric acid and the calculated amount of paraformaldehyde, was stirred vigorously and maintained at a temperature of approximately 70°, while a rapid stream of hydrogen chloride was passed through it. With *p*-xylene the reactions were completed in less than ten hours; with *m*-xylene in about one-third of that time. When cold, the organic layer was removed from the reaction mixture, washed with warm water, dilute sodium bicarbonate solution, and warm water again, to remove hydrochloric acid and any excess of paraformaldehyde, dried over calcium chloride, distilled and rectified under diminished pressure.

Where solid products were formed, as in the preparation of the dichloromethyl derivatives, the reaction mixture was taken up first in boiling toluene, then filtered, washed and distilled, as in the other cases. The residual solids were purified by one crystallization from 95% ethanol, followed by recrystallization from "Skelly-solve D" (an unsaturate-free petroleum fraction, b. p. 77–115°), until the m. p. remained constant.

2,4-Dimethylbenzyl Chloride (II).—Yield 61%; b. p. 116–118° at 16 mm., as recorded by Bogert and Stamatoff,[3] and 86–87° at 7 mm. Blanc[10] reported the b. p. as 115° at 15 mm.; von Braun and Nelles[11] as 100–105° at 14 mm.

2,5-Dimethylbenzyl Chloride (II).—Yield, up to 90%; b. p. 100.5–101.5° at 15 mm., 86–87° at 7 mm. Bardhan and Sengupta[4] gave the b. p. as 86–87° at 7 mm., and von Braun and Nelles[11] as 100–103° at 12 mm.

Anal. Calcd. for $C_9H_{11}Cl$: C, 69.88; H, 7.17. Found: C, 70.09, 69.70; H, 7.04, 6.96.

Like benzyl chloride itself, these liquid methylated benzyl chlorides are quite sensitive to hydrolyzing agents, are powerful lachrymators, and function as solvents for the higher chloromethylated products.

2,5-*Bis*-(chloromethyl)-*p*-xylene (III).—Beautiful long white needles, m. p. 132° (corr.); von Braun and Nelles[11] found 133°. Yield, 72 g. from 106 g. of *p*-xylene.

Anal. Calcd. for $C_{10}H_{12}Cl_2$: C, 59.11; H, 5.96. Found: C, 59.28, 59.24, 59.12; H, 6.29, 6.15, 5.86.

This compound had been prepared and its constitution established by oxidation to pyromellitic acid, when the appearance of the paper by von Braun and Nelles[11] rendered further work in this direction unnecessary.

From the chlorides (II), the cyanides were prepared by refluxing in dilute alcoholic solution with sodium cyanide and purifying by fractionation under reduced pressure.

2,4-Dimethylbenzyl Cyanide (IV).—B. p. 140° at 11 mm., as found by Bogert and Stamatoff,[3] and 115–117° at 6 mm.

2,5-Dimethylbenzyl Cyanide (IV).—White solid, m. p. 28°, or colorless transparent mobile liquid, b. p. 142–143° at 19 mm., and 116–118° at 6 mm. Bardhan and Sengupta[4] gave the b. p. as 115–119° at 6 mm., and the yield as 66.5%. Our yield was 73%.

Anal. Calcd. for $C_{10}H_{11}N$: C, 82.70; H, 7.64. Found: C, 82.40; H, 7.25.

Ethyl 2,4-dimethylphenylacetate, prepared directly from the nitrile, via the imino ester, boiled at 113–115° at 4 mm. Harispe[12] reported it as 146.5° at 18 mm.

Ethyl 2,5-dimethylphenylacetate, prepared similarly from the corresponding nitrile, b. p. 114–116° at 4 mm., in agreement with the b. p. found by Bardhan and Sengupta.[4]

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.95; H, 8.39. Found: C, 75.22; H, 8.60.

***p*-Xylylacetic acid (2,5-dimethylphenylacetic acid) (V)**, from the nitrile and sulfuric acid, after two crystallizations from water, formed white needles, m. p. 129.5° (corr.); yield 80%. Guerbet,[13] and Büchner and Schulze,[14] who obtained this acid by other methods, recorded its m. p. as 128 and 128.9°, respectively.

Alpha-(*p*-Xylyl)-*o*-nitrocinnamic acid (VI) was obtained in the usual way, by the interaction of *o*-nitrobenzaldehyde, acetic anhydride and potassium *p*-xylylacetate. The crude product was crystallized twice from glacial acetic acid, digested twice with Norite in 95% ethanol, followed by three crystallizations from 70% acetic acid. The pure compound formed pale yellow crystals, m. p. 173.5–174° (corr.); yield 75%.

Anal. Calcd. for $C_{17}H_{15}O_4N$: C, 68.66; H, 5.09. Found: C, 68.40; H, 5.05.

Alpha-(*p*-Xylyl)-*o*-aminocinnamic acid (VII), secured by reduction of the nitro acid (VI) with ferrous hydroxide and ammonia, proved to be very unstable. Repeated crystallization from 80% methanol, gave tiny rosets of stout pale yellow needles, m. p. 199–200.5° (corr.) with decomposition; yield 74%. The compound changed so quickly in the air that no satisfactory analytical figures could be obtained. Combustions run on freshly prepared samples, showed rapid progressive decomposition. For the next step in the synthesis, therefore, this amino acid was always freshly prepared and kept under methanol until used.

1,4-Dimethylphenanthrene-10-carboxylic Acid (VIII).—Following the standard Pschorr procedure, the above amino acid (VII) was diazotized with alcoholic hydrogen chloride and amyl nitrite, and the diazo compound then decomposed by copper powder. From 9.3 g. of (VII), there was obtained 7.3 g. of crude (VIII). This crude

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[8] (a) E. Merck, German Patent, 439,988 (1927); *C. A.*, **23**, 611 (1929); (b) I. G. Farbenind. A.-G., French Patent, 639,252 (1927); *C. A.*, **23**, 3931 (1929); (c) Tschunkur and Eichler, U. S. Patent, 1,727,682 (1929); *C. A.*, **23**, 5196 (1929).

[9] Clarke and Taylor, THIS JOURNAL, **45**, 830 (1923).

[10] Blanc, *Bull. soc. chim.*, [4] **33**, 316 (1923).

[11] Von Braun and Nelles, *Ber.*, **67**, 1094 (1934).

[12] Harispe, *Ann. chim.*, [11] **6**, 249 (1936).

[13] Guerbet, *Compt. rend.*, **125**, 36 (1897).

[14] Büchner and Schulze, *Ann.*, **377**, 281 (1910).

acid was digested twice in diluted ethanol solution with Norite, and was then obtained, by concentration of the solvent, in yellow plates. From 80% methanol, it crystallized in sparkling transparent platelets, with a yellowish tinge, and after three crystallizations the melting point remained constant at 199.7–200.2° (corr.); yield 85%; quite soluble in chloroform, ethanol, or acetic acid.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.56; H, 5.64. Found: C, 81.40; H, 5.74.

Hemipicrate.—Reddish-orange needles, m. p. 148.5–149° (corr.), in which two molecules of the carboxylic were combined with one of the picric acid.

Anal. Calcd. for $C_{40}H_{31}O_{11}N_3$: C, 65.82; H, 4.29; N, 5.76. Found: C, 66.01; H, 4.26; N, 5.68.

No other picrate was encountered.

1,4-Dimethylphenanthrene (**IX**).—The above acid (VIII) was decarboxylated by heating with quinaldine for fifteen minutes in the presence of copper powder or basic copper carbonate, following the technique of Fieser, Fieser and Hershberg,[15] who used quinoline instead of quinaldine. The crude distilled product was decolorized with Norite and crystallized from methanol, when it was obtained in glistening white fine needles, m. p. 50–51° (corr.); yield 90%. Decarboxylated by direct heating with copper powder alone, the melting point of the purified product was likewise 50–51° (corr.), but the yield only 77%.

Anal. Calcd. for $C_{16}H_{14}$: C, 93.15; H, 6.85. Found: C, 92.77; H, 6.88.

Picrate.—Scarlet plates (from methanol), m. p. 147–148°.

Anal. Calcd. for $C_{22}H_{17}O_7N_3$: C, 60.94; H, 3.96. Found: C, 60.63; H, 3.99.

Decomposed by sodium bicarbonate solution, the hydrocarbon was regenerated, m. p. 50–51° (corr.).

Styphnate.—Orange crystals, m. p. 135.5–136.5° (corr.).

Anal. Calcd. for $C_{22}H_{17}O_8N_3$: C, 58.51; H, 3.80; N, 9.31. Found: C, 58.82; H, 4.06; N, 9.26.

Quinone.—Attempts to obtain this by direct oxidation of the hydrocarbon, or of its 10-carboxylic acid, following the usual methods, proved fruitless. It was therefore partially hydrogenated by the action of sodium upon its isoamyl alcohol solution, and this crude reduction product then oxidized with potassium dichromate, in acetic acid solution. From 3 g. of the hydrocarbon, there were thus obtained a few orange plates which, after two crystallizations from a chloroform–methanol solution, melted at 214–216° (corr.).

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.32; H, 5.12. Found: C, 80.40; H, 5.09.

With phenylhydrazine, the compound reacted with formation of a product less soluble in dilute alcohol than the original material. The amount of quinone isolated, however, was insufficient for further purification of the quinone itself or of its phenylhydrazone.

Bardhan and Sengupta[4] took the crude distillate (2 g.) of their octahydro derivative (XI), b. p. 170–174° at 4 mm., and heated it for twenty hours with selenium (6 g.) at 300–320°. The crude product was converted into the picrate, which formed small orange needles, m. p. 155°, difficultly soluble in ethanol. The hydrocarbon, regenerated from the picrate, crystallized from methanol in long needles, m. p. 77°, and they reported it as the 1,4-dimethylphenanthrene. These melting points, as mentioned in the introductory portion of this paper, correspond closely with the figures reported by Bogert and Stamatoff,[3] and by Haworth, Mavin and Sheldrick,[5] for the 1,3-dimethylphenanthrene, and do not at all agree with figures given above for the product of our Pschorr synthesis.

The Action of Selenium upon 1,4-Dimethylphenanthrene.—The sample of 1,4-dimethylphenanthrene employed was of high purity. It was intimately mixed with finely powdered selenium, in the proportion of 1 g. of the former to 2.16 g. of the latter, and the mixture was heated for twenty-one hours at 310–320°, thus duplicating closely the experimental conditions followed by Bardhan and Sengupta[4] in the preparation of their dimethylphenanthrene.

Some decomposition of the hydrocarbon occurred and some hydrogen selenide was formed, but 94% of the original compound was recovered as the crude picrate (m. p. 144–146°, corr.) which, on purification, melted at 147–148° (corr.), and showed no depression in melting point when mixed with an authentic sample of 1,4-dimethylphenanthrene picrate, but a very considerable depression with the 1,3-dimethyl isomer.

Hence, no detectable rearrangement was caused by this selenium fusion.

Summary

1. 1,4-Dimethylphenanthrene has been synthesized from *p*-xylene by the Pschorr reaction, and found to be quite different from the product assigned this constitution by Bardhan and Sengupta.

2. Evidence is submitted which indicates that the Bardhan and Sengupta compound was probably the 1,3-isomer, and that migration of one of the methyl groups occurred during the high temperature fusion with selenium in the final step of their synthesis. So far as we are aware, this is the first case in phenanthrene chemistry where such a migration has been observed in a purely aromatic cycle.

3. The important bearing such molecular rearrangements have upon the determination of structures by selenium dehydrogenations, is pointed out.

NEW YORK, N. Y. RECEIVED APRIL 22, 1937

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[15] Fieser, Fieser and Hershberg, THIS JOURNAL, **58**, 2324 (1936).