complex mixtures, fractions 2, 3 and 4 (n_D, 1.5930, 1.5930, 1.5927) were combined and fractionated under very high reflux at 70 mm. to yield the constant volume (4 ml.) fractions shown in Table II.

TABLE II

Fraction	$n^{25}D$	Picrate, m.p., °C.	Fraction	$n^{25}D$	Picrate, m.p., °C.
1	1.5823	Not prepd.	8	1.5932	240 dec.
2	1.5885	240 dec.	9	1.5937	200–207
3	1.5896	245 dec.	10	1.5940	241–243
4	1.5908	243 dec.	11	1.5948	220–222
5	1.5916	237–239 dec.	12	1.5950	252–253
6	1.5921	241 dec.	13	1.5950	210–215
7	1.5929	245 dec.	Residue		

This table is presented to indicate the wide range of melting points of the picrates obtained from these cuts. Of the known quinoline and isoquinoline homologs none has been reported with a picrate melting as high as 245° so a number of the picrates shown must be those of bases not previously isolated from petroleum or converted to picrate after synthesis. The picrates from cuts 2 and 8 showed no depression in mixed melting point so these and intervening cuts were combined and studied. The main base was not identical with any known base and the amount liberated from 18 g. of purified picrate did not permit the extensive degradation that would be needed before deciding what base should be synthesized and compared with the shale-oil base.

Similar fractionation of neutralization cuts 9, 10 and 11 yielded another series of fractions all of which could easily be converted to solid picrates but only the well known, 2,3,8-trimethylquinoline could be identified. A number of other apparently pure picrates were obtained but none were identified.

The identity of 2,3,8-trimethylquinoline was established by analysis and by comparison of its properties with those of the compound reported by Poth, *et al.*[18] (calculated or previously reported properties in parentheses): m.p. 51–52° (55–56°); equivalent weight, non-aqueous titration, 171.5 (calcd. 171.23); % N, micro-Dumas, 8.23 (calcd., 8.19); m.p. picrate, 242–243° (243°); sulfate, 275° dec. (275° dec.). Mixed melting points were not depressed below the lower values.

In the search for the $C_{16}H_{25}N$, chloroform layer base 530 ml. of bases isolated from the chloroform phase were distilled from a Claisen flask, yield 480 ml. of bases, 50 ml. of tar. Careful fractionation through the spinning band column at 75 mm. pressure yielded 29 equal volume cuts and a 20-ml. tarry residue. The boiling range was 265 to 308° and the index of refraction range to 1.5200 at cut 18 and a final value of 1.5360.

The C_{16} base from petroleum has b.p. 278°; $n^{20}D$ 1.5129; and picrate m.p. 151°. Fractions 5 and 6 were selected as the ones that should contain the highest concentration of the base, if present, and attempts were made to isolate the solid picrate, hydrochloride, or acid sulfate, by the various methods employed by Bailey and students[18,19,20] in their prolonged study of this base. Many of their fractions were less highly fractionated than the shale-oil base at this stage but no solid derivative could be isolated. Similar tests on California petroleum base fractions yielded the solid derivatives without difficulty. Since a base b.p. 278° might be expected to be present in highest concentration in fractions somewhat lower boiling than fractions 5 and 6, another worker, Tom Cheavens, studied cuts 2 to 4 and again was unable to isolate a solid derivative, so it must be concluded that this interesting base, if present in shale-oil bases, is present in very low concentration or is mixed with types of bases from which it cannot be obtained in the form of solid derivatives without extensive additional fractionation probably by different methods.

Acknowledgment.—The authors wish to thank General Aniline and Film Corporation for supporting this work through fellowships from 1950–1953, and securing the generous supply of material for study.

(18) E. J. Poth, *et al.*, THIS JOURNAL, **52**, 1239 (1930).

(19) W. C. Thompson and J. R. Bailey, *ibid.*, **53**, 1002 (1931).

(20) B. F. Armendt and J. R. Bailey, *ibid.*, **55**, 4145 (1933).

AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Cyclization of Nitriles: A New Route to Some Phenanthrylamines[1-3]

BY C. K. BRADSHER, E. D. LITTLE AND DOROTHY J. BEAVERS

RECEIVED NOVEMBER 19, 1955

In the presence of concentrated sulfuric acid, (2-biphenylyl)-acetonitrile (VI, R = H), as well as certain α-alkyl and α-aroyl derivatives, undergo cyclization readily to yield the isomeric 9-phenanthrylamines (VII). A compound previously described as 9-(*p*-methoxyphenyl)-10-phenanthramide (IIIA) has been shown to be 10-(*p*-methoxybenzoyl)-9-phenanthrylamine (III).

In earlier work[4] it was shown that α-(*p*-methoxybenzoyl)-α-(*o*-biphenylyl)-acetonitrile (I) in the presence of concentrated sulfuric acid underwent conversion to an isomeric product. This product from analogy to the behavior of the phenyl analog of I (I, R = H) and from a consideration of certain features of the absorption spectrum, appeared to be IIIA.

As part of a program for the synthesis of 9-phenylphenanthrene derivatives[5] it seemed desirable to prepare a sample of the isomeric 9-(*o*-methoxyphenyl)-10-phenanthramide (IVA).

The acylation of (2-biphenylyl)-acetonitrile with methyl *o*-methoxybenzoate afforded II in 46% yield. When II was dissolved in concentrated sulfuric acid at 0° and allowed to remain at this temperature for three hours, a product having the composition expected for IVA was obtained in a yield of 85%. A sample of the new product was refluxed with hydrobromic and acetic acids with the idea that ether cleavage and hydrolysis might yield the lactone of 9-(*o*-hydroxyphenyl)-10-phenanthroic

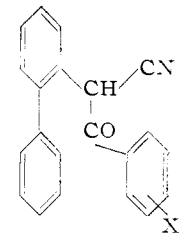
(1) This work has been the subject of a preliminary communication, THIS JOURNAL, **76**, 948 (1954).

(2) This investigation was supported by a research grant (C-1743) from the National Cancer Institute of the National Institutes of Health, Public Health Service.

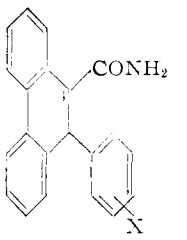
(3) Abstracted in part from theses submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (D.J.B.) and Master of Arts (E.D.L.).

(4) C. K. Bradsher and R. S. Kittila, THIS JOURNAL, **72**, 277 (1950).

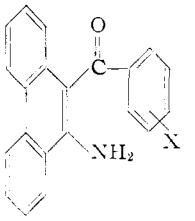
(5) Triphenylethylene derivatives, some of which have been found active as tumor necrotizing agents (*e.g.*, G. M. Badger, L. A. Elson, A. Haddow, C. L. Hewett and M. Robinson, *Proc. Roy. Soc.* (*London*), **B130**, 255 (1941)), may be regarded as "open" models of 9-phenylphenanthrene derivatives.



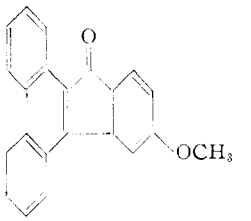
I, X = *p*-OCH_3
II, X = *o*-OCH_3



IIIA, X = *p*-OCH_3
IVA, X = *o*-OCH_3



III, X = *p*-OCH_3
IV, X = *o*-OCH_3



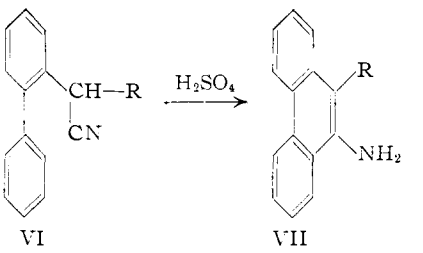
V

acid. Actually a mixture was obtained from which the only product identified was salicylic acid. Clearly the cleavage of salicylic acid from a molecule having the structure IVA would be very unlikely. An alternate possibility was that the nitrile rather than the carbonyl group of II had undergone an acid-catalyzed reaction with the adjacent phenyl nucleus yielding 9-amino-10-(*o*-methoxybenzoyl)-phenanthrene (IV). In support of this formulation for IV, it was observed that an acetic acid solution could be diazotized to give a positive diazonium coupling test with β-naphthol.

These observations led to a reconsideration of the structure IIIA assigned earlier[4] to the cyclization product obtained from I. It had already been demonstrated that this product reacted with nitrous acid to yield an unknown compound having the composition expected for $C_{22}H_{14}O_2$. It has now been found that the product from I gives a characteristic diazonium coupling test. In the light of this, the product from I must be represented as III rather than IIIA. The ability of diazotized derivatives of 2-aminobenzophenone to undergo cyclization[6] to yield fluorene derivatives suggests that the previously unidentified product ($C_{22}H_{14}O_2$) obtained from III by the action of nitrous acid is 1,2,3,4-dibenzo-6-methoxyfluorenone (V).

A logical extension of the new cyclization reaction would be its application to simple α-(2-biphenylyl)-nitriles (VI). Although the first member of this series (R = H) has been known for several years[7] there is no record of a cyclization being attempted. When 2-biphenylylacetonitrile (VII, R = H) was dissolved in concentrated sulfuric acid and allowed to stand at 0° for three hours, yields of 72–85% of 9-phenanthrylamine (VII, R = H) were obtained.

Some of the homologs of 2-biphenylylacetonitrile (VI, R = H) have been prepared from it by alkylation using sodium amide and an alkyl halide.[8]



VI VII

The results obtained in the cyclization of these to yield 9-alkyl-10-phenanthrylamines (VII) are summarized in Table I.

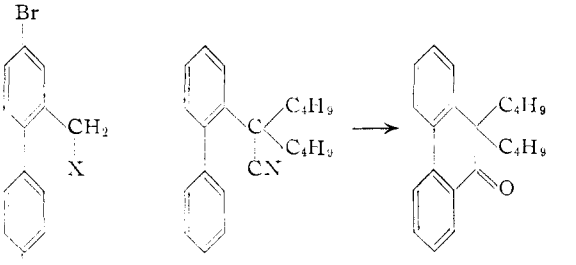
TABLE I

PHENANTHRYLAMINES (VII) BY CYCLIZATION OF NITRILES

R	Yield,[a] %	Amine	M.p.,[b] °C. hydrochloride	Benzamide
H	72–85	138–138.5[c]	278 (dec.)[d]	199–201[e]
CH_3	61	148.5–150	275.5–277	251–252
C_2H_5	83	117.5–119.5	268–270	241–243
C_3H_7	74	101–102.5	250.5–252	220–221.5
C_4H_9	62	70.5–72	275–277	.....[f]

[a] Yields are of products melting within 3.5° of the analytical sample. [b] Reported melting points are for analytical samples. [c] Reported 137.5–138° by L. F. Fieser, R. P. Jacobson and C. C. Price, THIS JOURNAL, **58**, 2163 (1936). [d] Reported *ca.* 275° dec. by J. Schmidt and M. Strobel, *Ber.*, **34**, 1461 (1901). [e] Reported 199° by W. E. Bachmann and C. H. Boatner, THIS JOURNAL, **58**, 2097 (1936). [f] Converted to the dibenzoyl derivative, m.p. 171–172°.

Although no effort was made to find the optimum conditions for each cyclization, the yields were quite good for the compounds listed. If α-(2-biphenylyl)-β-phenylpropionitrile (VI, R = $C_6H_5CH_2$), was subjected to the usual cyclization conditions sulfonation appeared to be the chief reaction. A similar observation was made with 2-phenyl-4-methoxybenzyl cyanide.[9] On the other hand (4,4′-dibromo-2-biphenylyl)-acetonitrile[10] (VIII) in which the aromatic rings are strongly deactivated failed to cyclize, and gave instead the corresponding amide IX.[10]



VIII, X = CN
IX, X = $CONH_2$

X XI

Dialkylation of biphenylylacetonitrile (VI), R = H) with butyl bromide afforded a nitrile X which on cyclization in the usual way gave the known[11] 10,10-dibutyl-9-keto-9,10-dihydrophenanthrene (XI).

The new cyclization reaction is clearly an intra-

(6) C. Graebe and F. Ullmann, *Ber.*, **27**, 3483 (1894); F. Ullman and H. Bleier, *ibid.*, **35**, 4273 (1902).

(7) J. von Braun and G. Manz, *Ann.*, **468**, 258 (1929).

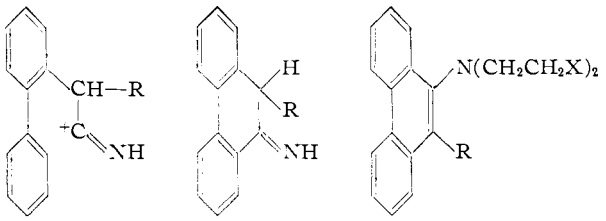
(8) C. K. Bradsher and W. J. Jackson, Jr., THIS JOURNAL, **73**, 3235 (1951); *ibid.*, **76**, 734 (1954).

(9) C. K. Bradsher and W. J. Jackson, Jr., *ibid.*, **74**, 4880 (1952).

(10) C. K. Bradsher and L. E. Beavers, unpublished results.

(11) E. J. H. Chu and Z. I. Shen, *J. Chinese Chem. Soc.*, **10**, 116 (1943); *C. A.*, **38**, 2953 (1944).

molecular counterpart of the Hoesch reaction[12] and probably involves the formation of a conjugate acid XII which cyclizes through electrophilic attack on the adjacent phenyl group. The imine XIII first formed tautomerizes rapidly to the stable aromatic system VII.[13]



XII XIII XIV

The major differences between this cyclization and the usual Hoesch reaction are (1) no Lewis acid is used[14]; (2) the aromatic nucleus does not need to be highly activated as by the presence of methoxyl or hydroxyl groups[15] and (3) in the use of concentrated sulfuric acid instead of hydrogen chloride as the cyclizing agent.[16] These differences are further indications of the lower degree of activation required for cyclizations as compared with intermolecular reactions.

Two of the new 9-alkyl-10-phenanthrylamines (VII, R = CH_3, C_3H_7) were converted to the corresponding N,N-bis-2-chloroethyl derivatives or "nitrogen mustards" (XIV, X = Cl) *via* the N,N-bis-2-hydroxyethyl analogs (XIV, X = OH).[17]

Experimental

α-(*o*-Methoxybenzoyl)-α-(*o*-biphenylyl)-acetonitrile (II).[4]—To a suspension of sodium amide (prepared from 1.5 g. of sodium) in dry ether was added 9.6 g. of 2-biphenylylacetonitrile in 20 ml. of ether. When this addition was complete 8.8 g. of methyl *o*-methoxybenzoate in 20 ml. of ether was added dropwise with vigorous stirring. The solution was refluxed with continued stirring for three additional hours. After the reaction mixture had stood overnight the thick suspension was poured on ice, acidified and extracted with ether. Concentration of the ethereal solution and crystallization of the residue from ethyl alcohol gave 7.5 g. (46%) of small rectangular white plates suitable for further reactions.

An analytical sample was recrystallized from alcohol, m.p. 137–138.5°.

Anal. Calcd. for $C_{22}H_{17}NO_2$: C, 80.79; H, 5.20. Found: C, 80.58; H, 5.28.

9-Amino-10-(*o*-methoxybenzoyl)-phenanthrene (IV).—Two grams of the ketonitrile (II) was dissolved in 20 ml. of concentrated sulfuric acid cooled in an ice-bath. After stirring for three hours the lemon yellow solution was poured on ice and the bright yellow solid collected, washed with sodium bicarbonate solution and dried to yield 1.7 g. (85%) of material, m.p. 170–173°. The analytical sample, prepared by recrystallization from chloroform consisted of colorless prisms, m.p. 175–176°.

Anal. Calcd. for $C_{22}H_{17}NO$: C, 80.74; H, 5.19. Found: C, 80.82; H, 5.10.

A sample of the product diazotized in acetic acid solution gave a red coupling product with alkaline 2-naphthol.

Action of Hydrobromic Acid on 9-(*o*-Methoxybenzoyl)-10-aminophenanthrene (IV).—One-half gram of IV was dissolved in a mixture containing equal parts of acetic and 48% hydrobromic acids and refluxed for 24 hr. The cooled mixture was diluted and extracted with ether, a small quantity of an insoluble material being removed by filtration[18] and the ethereal layer concentrated. Sublimation of the residue afforded 0.09 g. (43%) of nearly pure salicylic acid, m.p. 156–157°, which did not depress the melting point of an authentic sample.

Preparation of Nitriles VI.—The known nitriles (VI, R = H, CH_3, C_2H_5, C_3H_7) were prepared as described previously.[8]

α-(2-Biphenylyl)-capronitrile (VI, R = C_4H_9).—A suspension of sodium amide[19] (from 1.37 g. of sodium) in ether was treated with 10 g. of biphenylylacetonitrile (VI, R = H) and after stirring for 0.5 hr., 6.7 ml. of *n*-butyl bromide was added (exothermic reaction). The mixture was refluxed for 1 hr. and stirring was continued overnight at room temperature. Worked up in the usual way, 7.3 g. (58%) of a viscous yellow oil, b.p. 150.5–151° (0.5 mm.), was obtained. The analytical sample had b.p. 151° (0.5 mm.); $n^{24.5}D$ 1.5524.

Anal. Calcd. for $C_{18}H_9N$: C, 86.70; H, 7.68. Found: C, 86.59; H, 7.68.

α-(2-Biphenylyl)-α-(*n*-butyl)-capronitrile (X).—The alkylation of 10 g. of α-(2-biphenylyl)-acetonitrile was carried out as above except that sodium amide from 2.74 g. of sodium and 14 ml. of butyl bromide were used. The product consisted of 10.3 g. (65.5%) of a very viscous yellow oil, b.p. 164–174° (1.5–2 mm.), which on standing solidified to large white elongated prisms. The analytical sample was crystallized from methanol; m.p. 60–61.5°.

Anal. Calcd. for $C_{22}H_{27}N$: C, 86.50; H, 8.91. Found: C, 86.64; H, 8.82.

α-(2-Biphenylyl)-β-phenylpropionitrile (VI, R = $C_6H_5CH_2$) was prepared from 10 g. of α-(2-biphenylyl)-acetonitrile by alkylation with 7.4 ml. of benzyl bromide in a manner similar to that used in the preparation of the butyl analog (VI, R = butyl). The product was obtained as a viscous yellow oil, b.p. 175–185° (1–2 mm.). The analytical sample had b.p. 182–185° (1 mm.).

Anal. Calcd. for $C_{21}H_{17}N$: C, 89.01; H, 6.08. Found: C, 88.97; H, 6.17.

Cyclization Procedure.—The usual procedure was to dissolve the nitrile VI in concentrated sulfuric acid (10 ml. per gram of nitrile) at 0° and to maintain the greenish mixture at this temperature for 3 hr. At the end of this period the solution was poured on crushed ice with rapid stirring. The pale yellow phenanthrylamine salt was collected, dissolved in a minimum quantity of hot alcohol and neutralized

TABLE II

PHENANTHRYLAMINES

VII, R =	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
CH_3	$C_{15}H_{13}N$	86.92	87.02	6.32	6.35
C_2H_5	$C_{16}H_{15}N$	86.84	86.79	6.83	7.08
C_3H_7	$C_{17}H_{17}N$	86.77	86.56	7.28	7.35
C_4H_9	$C_{18}H_9N$	86.70	86.65	7.68	7.73

(12) P. E. Spoerri and A. S. DuBois, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 387. The authors point out (p. 395) that attempts to carry out intramolecular Hoesch reactions have met with very limited success. Examples in which a new heterocyclic ring was established in such a cyclization may be seen in papers by W. Baker, A. Pollard and R. Robinson, *J. Chem. Soc.*, 1468 (1929), and by I. Badhwar and K. Venkataraman (*ibid.*, 2420 (1932)).

(13) Where tautomerism is impossible, as in the case of the cyclization product from X, hydrolysis of the imine occurs readily.

(14) Zinc or aluminum chlorides are usually used in conjunction with hydrogen chloride. Although these catalysts are beneficial (*cf.* J. Houben and W. Fischer, *Ber.*, **60B**, 1759 (1927)), some active aromatic nuclei undergo condensation without them.

(15) Aromatic hydrocarbons such as benzene or toluene condense only with very reactive nitriles such as trichloroacetonitrile and apparently only in the presence of an aluminum chloride catalyst (J. Houben and W. Fischer, *J. prakt. Chem.*, **123**, 89 (1929)).

(16) There have been isolated reports of the use of sulfuric acid in the Hoesch reaction (*e.g.*, B. N. Ghosh, *J. Chem. Soc.*, **109**, 105 (1916)), but the ease with which phenols and ethers undergo sulfonation would suggest that sulfuric acid would be, in general, less useful.

(17) Dr. Howard E. Skipper of the Southern Research Institute has graciously consented to test the two nitrogen mustards (XIV, R = CH_3 or C_3H_7, X = Cl) and one of the bis-2-hydroxyethyl derivatives (XIV, R = CH_3, X = OH) for activity against sarcoma 180 in mice. The results of these tests will be reported elsewhere.

(18) This ether-insoluble material which yielded 0.05 g. of white crystals, m.p. 181–183°, from ethanol was not identified.

(19) Sodium ethoxide was found to be ineffective in this alkylation.

by the addition of a concentrated solution of sodium carbonate. After filtering off the sodium sulfate the alcohol solution was concentrated, diluted with water to the point of incipient turbidity and crystallized. The resulting material was usually recrystallized from either dilute or 95% ethanol. Yields and melting points are reported in Table I, analyses in Table II.

Amine hydrochlorides were usually prepared by addition of hydrogen chloride to an ethereal solution of the amine. Melting points are reported in Table I, analyses in Table III.

TABLE III

PHENANTHRYLAMINE HYDROCHLORIDES

VII, R =	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
CH_3	$C_{15}H_{14}NCl$	73.92	73.46	5.79	5.86
C_2H_5	$C_{16}H_{16}NCl$	74.55	74.40	6.26	6.67
C_3H_7	$C_{17}H_{18}NCl$	75.12	75.10	6.68	6.79
C_4H_9	$C_{18}H_{20}NCl$	75.64	75.55	7.05	7.06

Benzamide derivatives of VII were prepared by the action of benzoyl chloride in a mixture of benzene and dry pyridine. Melting points are given in Table I and analyses in Table IV. All derivatives formed white needles, the usual solvent being benzene–hexane.

TABLE IV

BENZOYL DERIVATIVES

Of VII, R =	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
H	$C_{21}H_{15}NO$	84.82	85.11	5.09	4.98
CH_3	$C_{22}H_{17}NO$	84.86	85.18	5.50	5.51
C_2H_5	$C_{23}H_{19}NO$[a]	84.89	85.00	5.89	5.93
C_3H_7	$C_{24}H_{21}NO\cdot H_2O$	80.64	80.70	6.49	6.42
C_4H_9	$C_{32}H_{27}NO_2$[b]	84.00	83.74	5.95	5.98

[a] Crystallized from ethanol. [b] The dibenzamide was obtained under the more drastic conditions used in this experiment.

10,10-Dibutyl-9-keto-9,10-dihydrophenanthrene (XI).—Concentrated sulfuric acid (100 ml.) was cooled in an ice-bath and 7.75 g. of α-(2-biphenylyl)-α-butylcapronitrile (X) added with stirring. Stirring was continued for 3 hr. at 0° and the green solution poured on ice. The resultant gummy solid neutralized and recrystallized from dilute ethanol yielded 6.32 g. (81.5%) of pale yellow needles, m.p. 69–71°. An analytical sample was obtained as long white needles from methanol; m.p. 72–72.5° (lit.[11] 71.8–72.8°).

Anal. Calcd. for $C_{22}H_{26}O$: C, 86.23; H, 8.55; mol. wt., 306. Found: C, 85.89; H, 8.47; mol. wt. (by b.p. elevation in acetone), 318.

Sodium fusion showed nitrogen to be absent, while the presence of the carbonyl group was indicated by a strong infrared absorption at 5.94 μ.

Attempted Cyclization of α-(2-(4,4'-Dibromo)-biphenylyl)-acetonitrile (VIII).—Two grams of the nitrile VIII[10] was shaken vigorously with 40 ml. of concentrated sulfuric acid. Solution took place slowly. After the yellow solution had stood in the ice-bath for a total of 19 hr. and at room temperature for 5 hr., the solution was poured on ice and worked up in the usual way. The product consisted of 1.47 g. (70%) of beautiful white needles (m.p. 215.5–217°) which did not depress the melting point of an authentic sample of α-(2-(4,4'-dibromo)-biphenylyl)-acetamide (IX).[10]

N,N-Bis-(2-hydroxyethyl)-10-methyl-9-aminophenanthrene (XIV, R = CH_3, X = OH).—Five grams of 10-methyl-9-phenanthrylamine (VII, R = CH_3) was heated in a sealed tube with 2.12 g. of ethylene oxide for 20 hours at 175–179°.[20] The resultant pale yellow oil was dissolved in 50 ml. of warm ethanol, treated with Darco and Hyflo and filtered. The solution crystallized after standing for one week. Recrystallization of the crude solid from dilute alcohol yielded 3.38 g. (47.5%) of white platelets, m.p. 144.5–146°. The analytical sample melted at 144–145.5.

Anal. Calcd. for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17 Found: C, 76.97; H, 6.99.

N,N-Bis-(2-chloroethyl)-10-methyl-9-aminophenanthrene (XIV, R = CH_3, X = Cl).—A portion of the bis-(hydroxyethyl)-amine (XIV, R = CH_3, X = OH) above (1.90 g.) was placed with 3 ml. of phosphorus oxychloride in a 50-ml. flask provided with a mechanical stirrer and reflux condenser and protected by calcium chloride drying tubes. The mixture was heated gently on the steam-bath giving a clear yellow solution. After 3.5 hr., although hydrogen chloride was still being evolved, the chloride was poured cautiously into benzene and ice-water. The water was separated and washed with more benzene. The hydroxyethylamine (starting material) being more basic than the expected chloroethylamine (product) would be expected to remain in the acidic water layer. The combined benzene extracts were dried over magnesium sulfate and then passed through a 5-cm. chromatographic column (activated alumina). Elution with benzene followed by concentration of the benzene solution and addition of ligroin (60–90°) afforded 1.05 g. (50%) of white prisms, m.p. 102.5–104° (sealed capillary). Three recrystallizations from ligroin gave 0.9 g. of cream-colored prisms, m.p. 100.5–102°.[21]

Anal. Calcd. for $C_{19}H_{19}NCl_2$: C, 68.68; H, 5.76; Cl, 21.34. Found: C, 69.39; H, 5.79; Cl, 20.40.

N,N-Bis-(2-chloroethyl)-10-propyl-9-aminophenanthrene (XIV, R = C_3H_7, X = Cl).—Ethylene oxide (1.88 g.) was heated in a sealed tube with 5 g. of 10-propyl-9-phenanthrylamine (VII, R = C_3H_7) at 175° for 20 hr. with continuous rocking. The dark red oil was dissolved in ethanol. The solution, filtered and diluted, gave on standing a white amorphous solid. Thrice recrystallized this afforded 2.79 g. of material melting at 121.5–127.5°. This substance was presumably the N,N-bis-(2-hydroxyethyl) derivative (XIV, R = C_3H_7, X = OH) and was used directly in the next step without further purification. A portion of this material (1.57 g.) was stirred on the steam-bath with 2.5 ml. of phosphorus oxychloride for 2 hr. and worked up as in the case of the homolog (XIV, R = CH_3, X = Cl). Once crystallized from ligroin it formed large white clusters of prisms, m.p. 109–111° (sealed capillary).

Anal. Calcd. for $C_{21}H_{23}NCl_2$: Cl, 19.68. Found: Cl, 19.40.

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(20) Due to failure of a thermocouple the temperature rose to 210–220° during one hour of the time.

(21) This material was very corrosive toward both cork and rubber stoppers and unstable toward light. Difficulty in manipulation of the material prevented its isolation in the highest state of purity.