Experimental

The generator was a Hypersonic Transducer Model BU 305A-600 (Brush Electronic Co., 8 amp., estimated power input 200 watts at 550–600 kilocycles). A barium titanate transducer element with a glazed finish was used.

Treatment of Pyridine.—A solution of 1 ml. of pyridine in 50 ml. of 0.05 N silver nitrate darkened after a few minutes of ultrasonic treatment and began to deposit a heavy precipitate. The treatment was continued for a total of 20 hr. At 5-hr. intervals the precipitate was removed by centrifugation, washed successively with water, alcohol, ether, then dried and weighed. The amount of the silver eliminated from the liquid phase was then determined approximately (the precipitates contained about 85% silver) and replaced by adding silver nitrate crystals. The four precipitate fractions were combined. (The aqueous filtrate was yellow and slightly acid.)

Treatment of Nicotine.—A freshly prepared solution of 1 ml. of nicotine in 50 ml. of 0.05 N silver nitrate was filtered after standing for 30 min. to remove a negligible amount of a black precipitate (1–2 mg.). The filtrate was then treated ultrasonically and the precipitate worked up in the manner described for pyridine.

Estimation of Cyanide.—The brownish-black precipitate was extracted thrice with 10-ml. portions of concentrated ammonia while vigorously shaking for 30 min. each time. After centrifugation[9] and washing, the brownish extract was diluted to 50 ml. in a volumetric flask. A 1-ml. or 2-ml. sample was then pipetted into a 15-ml. conical centrifuge tube and a 10% potassium iodide solution (about 5 drops) was added in slight excess in order to precipitate the silver. The suspension was made weakly acid with dilute nitric acid and the silver iodide was removed by centrifugation. The resulting solution was made basic with a few drops of 5% potassium hydroxide. Finally, 0.5 ml. of freshly prepared 3% ferrous sulfate was added, followed by the introduction of a small potassium fluoride crystal (about 50 mg.).[8] The liquid (the ferrous hydroxide precipitate included) was shaken to mix the reactants and was allowed to stand for 10 min. (in case of very small amounts of cyanide, for 25 min.). After acidification with dilute nitric acid, dilution with water to 10 ml. and vigorous shaking, the extinction of the (semi-colloidal) prussian blue was estimated at 750 $m\mu$ in a Beckman spectrophotometer, model DU. The values were compared with a calibration curve obtained by carrying out the operations described with known amounts of cyanide.

Estimation of Acetylene and Diacetylene.—The fraction that remained undissolved after the extraction of the silver precipitate with ammonia was converted into a mixture of cuprous acetylide and diacetylide as described earlier.[2] This was dissolved in acid ferric sulfate and titrated according to Willstätter and Maschmann.[6]

Details of the separation of acetylene tetrabromide and diacetylene hexabromide were given in our first report.[2] After recrystallization from chloroform (rather than from alcohol) the diacetylene hexabromide crystals melted at 182–183° (cor.) and did not give a depression with an authentic sample.

Acknowledgment.—Dr. S. C. Crane kindly helped us in maintaining and improving the ultrasonic equipment.

PASADENA, CALIFORNIA

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[9] Some difficulty was encountered in the centrifugation of these basic solutions; small losses of precipitate were observed.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

Some Colorado Shale-oil Bases[1]

BY H. L. LOCHTE AND H. W. H. MEYER[2,3]

RECEIVED OCTOBER 20, 1955

A combination of fractionation by distillation, by chloroform extraction of aqueous solutions of hydrochlorides, and by systematic fractional neutralization yielded Colorado shale-oil base fractions from which quinoline and isoquinoline and a series of methyl homologs were isolated and identified from material boiling from 227 to 239°, while similar separations of bases boiling from 264–290° yielded large amounts of 2,3,8-trimethylquinoline and a series of unidentified picrates but none of the very stable $C_{16}H_{25}N$ base found in high concentration in California petroleum bases. In general these shale-oil bases formed much larger amounts of tar than did corresponding California petroleum base fractions.

A number of investigators have studied the nitrogen compounds in various shale oils and shale-oil fractions. They have found that a considerable fraction of the compounds cannot be extracted with dilute acids and that these compounds, including pyrroles, seem to be responsible for the much greater tendency toward tar formation in various separation procedures than has been observed in working with petroleum bases. In this respect the shale-oil bases show greater similarity to low temperature coal tar bases than to petroleum bases.

A considerable amount of work has been done on the lower boiling shale-oil bases[4-10] and these studies have led to the identification of a number of simple alkylpyridines. Quinolines and isoquinolines have been mentioned and recently the U. S. Bureau of Mines workers[10] have reported the presence of quinoline and 2-methylquinoline on the basis of boiling point, index of refraction and ultraviolet absorption spectra. This group also isolated two pyrroles and three benzonitriles.

Quite recently Fushizaki[11] reported the isolation and identification of a series of alkylpyridines, quinoline, isoquinoline, 2-methyl- and 3-methylquinoline and probably several others from Manchurian shale-oil.

None of the higher boiling alkylquinolines, the alkylcyclohexylpyridine identified by Bailey[12,13]

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[1] Presented before the Petroleum Division at the American Chemical Society Meeting in Cincinnati, Ohio, March, 1955.

[2] General Aniline and Film Corporation Fellow, 1950–1952.

[3] From the Ph.D. Dissertation of H. W. H. Meyer, The University of Texas, 1953.

[4] G. E. Mapstone, *J. Proc. Roy. Soc. N.S. Wales*, **82**, 79 and 129 (1948).

[5] F. C. Garrett and J. A. Smythe, *J. Chem. Soc.*, **81**, 449 (1902).

[6] T. Eguchi, *Bull. Chem. Soc. Japan*, **2**, 172 (1927); **3**, 227 (1928).

[7] J. W. Horne, W. F. Finley and C. D. Hopkins, *U. S. Bur. of Mines*, Bull. No. 415 (1938).

[8] Report to the Sec. of Interior on Synth. Fuel Act from Jan. 1946 to Dec. 1946, p. 58–59.

[9] R. J. Benzie, J. N. Milne and H. B. Nisbet, "Oil Shale and Cannel Coal," Geo. Sell, Inst. of Petroleum, Manson House, London, 1951, Vol. II.

[10] R. A. Van Meter, C. W. Bailey, J. R. Smith, R. T. Moore, C. S. Allbright, A. Jacobson, V. M. Hylton and J. S. Ball, *Anal. Chem.*, **24**, 1758 (1952).

[11] Y. Fushizaki, *Tech. Repts. Osaka Univ.*, **1**, 310 (1951).

[12] C. M. Schenck and J. R. Bailey, THIS JOURNAL, **63**, 1365 (1941).

[13] W. Shive, S. M. Roberts, R. I. Mahan and J. R. Bailey, *ibid.*, **64**, 909 (1942).

nor the other bases boiling in the 270–280° range have been reported from shale-oil. It was the purpose of the present investigation to attempt to isolate the quinolines, isoquinolines and other bases in Colorado shale-oil boiling in the range 235–250° and to isolate some of the alkylquinolines and the interesting 2,4-dimethyl-6-(2,2,6-trimethylcyclohexyl)-pyridine isolated by Bailey's group from petroleum bases boiling between 270 and 290°.

The bases were isolated at Austin from one barrel of light gas oil furnished, through arrangements by General Aniline and Film Corporation, by the U. S. Bureau of Mines Shale Demonstration Plant near Rifle, Colorado. The distillate was produced by atmospheric pressure distillation of shale-oil at the Rifle refinery which reported a boiling range of 131–330° and found the distillate to contain 12.2% nitrogen bases and 4.4% organic acids by volume. Analyses at Austin showed that the nitrogen base content increased with increase in boiling point.

The main batch of 209 liters of distillate was extracted with 4 *N* sodium hydroxide to remove acidic compounds, then with dilute sulfuric acid to extract the basic compounds which were finally liberated by sodium hydroxide. The yield of washed and dried bases was 23 liters.

Efficient fractionation of an 800-ml. batch of the crude bases yielded data which show that (a) the crude bases boiled over a range that included both the bases boiling at 227–239° and those boiling at 264–300° which were the two ranges to be studied, and (b) the index of refraction of the series of fractions shows that the lowest boiling material consists probably mainly of simple alkylpyridines while the higher boiling fractions are rich in quinolines and/or isoquinolines. Since bases of unknown structure with an index of refraction intermediate between the pyridines and quinolines in unknown concentrations are present it is impossible to decide whether the alkylpyridines occur throughout the whole range.

Fractionation of the main batch through a 12 ft. packed column yielded 65 constant volume (200 ml.) cuts. Before the fractionation these bases contained 5.95% nitrogen; the residue in the still pot at the end of the fractionation contained 5.54% nitrogen.

Fractions boiling 227–239° were combined, converted to the hydrochlorides, and those in aqueous solution extracted with chloroform. Perrin and Bailey[14] found that this chloroform extraction procedure is a remarkably effective method of separating petroleum bases like quinolines with a high index of refraction from others like pyridines with a low index of refraction. The bases in the water layer were studied in this work.

Fractional neutralization of the quinoline type bases yielded a series of 16 fractions from which solid picrates usually could be obtained but not purified except with excessive losses. Two compounds, 7- and 8-methylquinoline were isolated at this stage. The weakest fractions—E 14, 15, 16—consisted mainly of tar.

The neutralization cuts were divided, on the basis of index of refraction, into three batches and fractionally distilled to three series of fractions from which easily purified picrates were obtained and quinoline, 2-, 7- and 8-methylquinoline, 2,8-dimethylquinoline, isoquinoline and 1- and 3-methyl isoquinoline were identified.

Since Bailey[12-14] succeeeded in isolating a number of alkylquinolines from the water layer obtained in the chloroform extraction of the hydrochlorides of petroleum bases boiling between 270 and 280° and especially because they isolated about 2 gallons of the very interesting and stable $C_{16}H_{25}N$ base, 2,4-dimethyl-5-(2,2,6-trimethylcyclohexyl)-pyridine, from the chloroform layer in this extraction it seemed desirable to study shale-oil bases to determine whether the same quinolines and, particularly, the same $C_{16}H_{25}N$ compound could be isolated. In view of its great stability it should have escaped pyrolysis at the temperature of the retorts. This compound could not be isolated so it appears that the $C_{16}H_{25}N$ base is either absent or present only in trace amounts in these shale-oil bases.

Experimental

Batch extraction of the acids and then of the bases from 209 l. of shale-oil distillate was carried out in a 5-gal. mixer stirred slowly to avoid emulsions. For each batch the aqueous layer was cross-extracted at least once with petroleum ether and the organic layer with water. Six liters of acids was obtained in the extraction with NaOH solution. Only 30 ml. of water-soluble steam-volatile bases was obtained from the final aqueous layers.

The extraction of bases was accomplished by contacting the acid-free material with 6 *N* H_2SO_4 and subsequently liberating the bases with NaOH. A total of 23 l. of dry bases was obtained from 209 l. of distillate.

To obtain accurate information in regard to the properties to be expected of the fractions obtained in fractionation of the main volume of bases, an 800-ml. aliquot was dried and 600 ml. of the dry bases very carefully fractionated through a 3 ft. spinning band column supplied with automatic reflux and vacuum control. The reflux ratio was kept constant at 20:1 and the pressure at 46 mm. to fraction 56 and at 4 mm. thereafter. After collection of 40 ml. of low boiling impurities the remaining base mixture was collected in 8-ml. constant-volume cuts.

Twenty-one liters of the crude base was then subjected to a preliminary rough fractionation from a 5-gal. steel still with 3 ft. column packed with Raschig rings. This operation was performed mainly to obtain preliminary fractions to be added successively to the tall steel still used for final fractionation and to remove high boiling tarry material and compounds which would form such material during fractionation. Two liters of tarry residue was obtained. The final fractions, D 1–65, were obtained as the nine preliminary cuts were added in order of boiling point to the 2-gal. still with adiabatic 12 ft. steel column packed with Berl saddles and operated with high reflux at 16–18 mm. pressure. Constant volume (200 ml.) fractions were collected and were found to have properties expected from results of the batch fractionation carried out previously.

Duplicate Kjeldahl nitrogen determinations gave the following results: extracted shale-oil, 0.093, 0.093%; crude bases, 6.88, 7.01%; residue from preliminary fractionation (3 ft. column) 5.53, 5.56%. All isolated and synthetic bases and many fractions were titrated routinely with acid using the excellent non-aqueous titration method of Fritz.[15,16]

To determine the nature of the compounds present in the fractions in which a mixture of alkylpyridines, quinolines and isoquinolines might be expected, distillation fractions D17, 23, 24, 25, and 27, boiling 227–239°, were combined, mixture n^{25}D, 1.5162. The mixture was acidified with hydrochloric acid and extracted four times with chloroform. Each chloroform layer was cross-extracted with water and the aqueous layers combined, concentrated and made

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[14] T. S. Perrin and J. R. Bailey, THIS JOURNAL, **55**, 4136 (1933).

[15] J. S. Fritz, *Anal. Chem.*, **22**, 1028 (1950).

[16] H. L. Lochte, P. F. Kruse and E. N. Wheeler, THIS JOURNAL, **75**, 4477 (1953).

TABLE I

IDENTIFICATION OF BASES ISOLATED

Base	Bases isolated from fraction	B.p., °C.	M.p., °C.	$n^{25}D$	Neut. equiv.	Picrate m.p., °C.	Chloro-platinate m.p., °C.	Foot-notes
Quinoline		238	. . .	1.6245	129.15	203	225–227	*a*
	Da, 1, 2, 3, 5 Db, 2; Dc, 3	. . .	. . .	1.6200	129.6	201.5	220–222	*b*
Isoquinoline		242	24.5	1.6148 1.6223	129.15	226 222	263 dec.	
	Da, 6, 7, 8, 9	. . .	10.0	1.6100	132.1	222–223	263 dec.	*c*
1-Methylisoquinoline		248	. . .	1.6145	143.2	231–233	. . . . .	
	Da, 10	. . .	. . .	. . . .	141.8	231–233	. . . . .	*d*
2-Methylquinoline		. . .	. . .	. . . .	143.2	191–192	. . . . .	*e*
	Da, 9; Db, 7	. . .	. . .	1.6091	145	193–194	. . . . .	*f*
3-Methylisoquinoline		. . .	64.7	. . . .	. . . .	199	. . . . .	*g*
	Db, 7	. . .	63.0	. . . .	. . . .	198–199	. . . . .	*h*
7-Methylquinoline		. . .	39	1.6148	143.2	237	223–224	
	Db, 9; E, 7	. .	30–35	1.6047	. . . .	236–237	223	*i*
8-Methylquinoline		247	. . .	1.6162	143.2	200	. . . . .	*j*
	E, 11; Dc, 6	. . .	. . .	1.6068	143.2	200	. . . . .	*k*
2,8-Dimethylquinoline		252–255	22.6 27.0	1.6022	157.2	183	. . . . .	
	Dc, 8		17–19	1.5981	155.5	181–183	. . . . .	*l*
Base	E, 2, 3, 4	236	. . .	1.6198	134.1	179–180	207 dec.	*m*
Base	Da, 2, 3, 4	232	. . .	1.5325	141	165–166	. . . . .	*n*

[a] Literature values from Beilstein's "Handbuch der Organischen Chemie," Springer Verlag, Berlin, 1942, 4th Ed., 2nd Suppl., Vol. XX. [b] All identifications are based on at least one mixed melting point of salts or derivatives and usually 2 or 3 such were used, in addition to physical properties and neutral equivalents. No mixed melting point was lower than that of either sample. [c] Present in much smaller amount than quinoline. [d] Isolated in very small amount. [e] Styphnate, m.p. 216–219°; trinitro-*m*-cresolate, m.p. 223°. [f] Styphnate, m.p. 216°; trinitro-*m*-cresolate, m.p. 221–222°. [g] Synthetic sample available from earlier work. Styphnate, m.p. 202°. [h] Styphnate, m.p. 201°. [i] Isolated in yield of only 0.85 g. of pure picrate. Sample was not distilled so m.p. and n_D values approximate. [j] Styphnate, m.p. 198° dec.; trinitro-*m*-cresolate, m.p. 197°. [k] Styphnate, m.p. 198° dec.; trinitro-*m*-cresolate, m.p. 203°. Also identified by identical X-ray diffraction curves of the picrates. [l] Yield pure picrate, 1.9 g.; perchlorate m.p. 189°. [m] Isolated in yield of more than 10 g. pure picrate; hydrochloride m.p. above 260°. [n] Hydrochloride, m.p. 175–176°.

strongly alkaline with sodium hydroxide to yield 247 ml. (24.7%) of bases, $n^{25}D$ 1.5494; the chloroform layer similarly yielded material with $n^{25}D$ 1.4950. These bases, presumably a mixture of alkylpyridines, were not studied further.

The water phase bases were then subjected to a 16 stage fractional neutralization in the bottle extractor[17] starting with the 247 ml. of bases, converting them to an aqueous solution of the hydrochlorides placed in bottle 1 and adding $^1/_{15}$ equivalent of sodium hydroxide solution. Two-hundred ml. of petroleum ether was added and the apparatus rotated for 15 min. The petroleum ether phase was then transferred to bottle 2 which, like the other 14 bottles, contained $^1/_{15}$ equivalent of 1:1 hydrochloric acid. Another $^1/_{15}$ equivalent of sodium hydroxide and 200 ml. of petroleum ether was added to bottle 1 and the apparatus rotated. At the end of each rotation period the petroleum ether layers were transferred to the next bottle while another $^1/_{15}$ equivalent of sodium hydroxide and 200 ml. of petroleum ether were added to bottle 1 until all of the base in bottle 1 had been liberated and transferred and each of the next eight bottles contained equilibrated layers of salt and base. An excess of sodium hydroxide and 200 ml. of petroleum ether were now added in succession to bottles 2 through 16 until all of the base had been removed from bottle 16 as petroleum ether solutions of free base. The first 3 layers so removed contained mainly tar, the other 13 were individually distilled to yield the base fractions and small amount of tar in each case. The cuts were numbered in order of decreasing strength, *i.e.*, cut E 1, strongest, and cut E 16, weakest. Most of the cuts now yielded solid picrates but only from cut E 7 (7-methylquinoline) and cut E 11 (8-methylquinoline) could pure picrates be identified and then in low yield due to losses in recrystallization.

Since the wide boiling range neutralization cuts could not be expected to give satisfactory yields of pure picrates, similar cuts were combined and fractionated very carefully through the spinning band column at high reflux. Combinations so fractionated were E 2, 3, 4, and E 5, 6, 7, and 8, and E 10, 11, and 12, and yielded cuts Da, 1–11; Db, 1–9; and Dc, 1–9, respectively. From these the bases shown in Table I were isolated.

Study of Bases Boiling 264–300°.—Distillation fractions 47 to 59, inclusive, boiling 264–300° (2.65 l.), were combined and converted to the hydrochlorides. Chloroform extraction of a dilute aqueous solution of the hydrochlorides was carried out by using 3.65 l. of 1:1 hydrochloric acid to acidify the batch of bases and extracting this with four 2.65-l. portions of chloroform. The chloroform layers were contacted in turn with one l. of water. The combined water layers yielded 280 ml. of bases, $n^{25}D$ 1.5873, and 50 ml. of tar. Since this seemed too small a volume for study the chloroform layers were extracted repeatedly with water to yield finally an additional 120 ml. of bases, $n^{25}D$ 1.5735. The chloroform layer bases showed $n^{25}D$ 1.5194.

The water-layer bases were next distilled from a Claisen flask to remove large amounts of tar but the fractions still turned dark rapidly so instead of carrying out the usual fractional neutralization next, careful fractional distillation at 100 mm. through the 36 in. spinning band column operating at high reflux was done. The first 5 fractions had $n^{25}D$ values of 1.5030, 1.5404, 1.5674 and 1.5722, and 1.5784; the other 21 fractions gradually increased in index of refraction to 1.5930. The boiling range of cut 4 was 265–271°, cut 7 was 277–282°, cut 11 was 282–285°, and that of cut 26 was 299–303°.

Distillation fractions 7 through 21 were then combined, volume 212 ml., $n^{25}D$ 1.5873, and subjected to 16 stage neutralization in the apparatus used previously. The 15 cuts obtained were individually distilled under vacuum to yield in each case about 15 ml. of clear base and 1–2 ml. of tarry residue. Maxima were found at fractions 2 and 3 (1.5930) and at fraction 10 (1.5885) in the index of refraction curve. Cuts 14 and 15 were again essentially all tar. Solid picrates were obtained from the first 10 fractions but 2,3,8-trimethylquinoline (cut 10) was the only base readily identified. Since the neutralization cuts were obviously

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(17) H. L. Lochte and W. G. Meinschein, *Petroleum Eng.*, C41 (March 1950).

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[13,19,20] 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.

AUSTIN, TEXAS

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[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).

[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

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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

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

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[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.