TABLE I

PROPERTIES OF STEELE'S *l*-ABIETIC ACID AND "SUBLIMED" *l*-ABIETIC ACID

	Steel's *l*-abietic acid	"Sublimed" *l*-abietic acid
M. p., °C.	158	150
M. p. after 1 recrystn. from EtOH, °C.	158	150
$[\alpha]^{25}D$ (5% in EtOH)	−75.5	−35.1
Acid no.	185.4	185.3
Sapn. no.	185.4	185.3
Calcd. acid no.	185.5	......
% C	79.24	79.32
% H	9.86	9.90
Calcd. % C	79.40	......
Calcd. % H	10.00	......
C_6H_5COCl color reaction	Indigo-blue	Indigo-blue

in marked contrast to the original acid which turned brown and opaque under these conditions. In xylene solutions, however, this difference was not apparent. Using the technique of Dupont and Lévy[4] it was found that both acids absorbed oxygen at practically the same rate and to the same degree.

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(4) Dupont and Lévy, *Bull. soc. chim.*, **47**, 60 (1930).

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Studies in the Phenanthrene Series. X. Naphthoquinolines[1]

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The skeleton of morphine consists of a phenanthrene nucleus and a nitrogen-containing ring. Neither in natural nor synthetic products is any other example known of such a condensed ring system as is found in the morphine group. As an approach to the preparation of compounds containing similar ring systems, which might exhibit morphine-like action, we have considered it advisable to include the synthesis of several naphthoquinolines and naphthoisoquinolines.[2]

This communication deals with the synthesis of a naphthoquinoline derived from 3-aminophenanthrene. Since the latter compound has been hitherto prepared practically only through a very tedious detour (phenanthrene sulfonic acid to hydroxyphenanthrene to aminophenanthrene),[3] we sought for a more feasible preparative method. Very recently Bachmann and Boatner[4] described in a preliminary form the preparation of 1-, 2-, and 3-aminophenanthrenes by the Beckmann rearrangement of the oximes of 1-, 2-, and 3-acetylphenanthrenes, emphasizing the practical usefulness of this procedure. We have, independently of these authors, prepared 2- and 3-aminophenanthrenes in the same way. We are withholding the preparative details until comparison with Bachmann and Boatner's procedure can be made.

By application of Skraup's synthesis to 3-aminophenanthrene, a naphthoquinoline of m. p. 106–107° was obtained. In spite of careful search, no other isomer could be found, which indicates that ring closure took place in only one direction. A tetrahydro derivative, obviously hydrogenated in the nitrogen-containing ring, was readily obtained by high pressure reduction, employing Chromite catalyst. By catalytic reduction under ordinary conditions, using platinum oxide catalyst, the same py-tetrahydronaphthoquinoline was formed together with a more highly hydrogenated compound which is most probably an octahydronaphthoquinoline. Since there is still some uncertainty in our minds as to the nature of the substance obtained by the Emde degradation of the methochloride of N-methyltetrahydronaphthoquinoline, the comparison of the degradation product with 2-[3-(dimethylamino)-*n*-propyl]-phenanthrene does not permit any conclusions as to whether the nitrogen-containing ring is attached in the 3,4- or 3,2-positions of the phenanthrene nucleus.

We intend to present this final structural proof together with analogous experiments on the 2- and 9-aminophenanthrenes respectively, in a following communication.

Experimental

Naphtho-(1,2-f)-quinoline or Naphtho-(2,1-g)-quinoline.—For the sake of simplicity we shall refer to this compound as "naphthoquinoline." It was prepared by Cohn's modified method of Skraup.[5] Thirty grams of 3-aminophenanthrene was added to a suspension of 4.5 g. of ferrous sulfate in 30 cc. of nitrobenzene, which was subsequently mixed with a solution of 9.1 g. of boric acid in 46 cc. of glycerol. Finally, 25 cc. of concentrated sulfuric acid was introduced in small portions to the thoroughly stirred mixture. The gray pasty mass was then transferred to an Erlenmeyer flask, kept in a water-bath for three hours, and finally heated on a hot-plate until it turned to

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(1) The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: the Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia and the University of Michigan.

(2) See also Benzofuroquinolines, Mosettig and Robinson, THIS JOURNAL, **57**, 902 (1935).

(3) Werner and co-workers, *Ann.*, **321**, 248 (1902).

(4) Bachmann and Boatner, THIS JOURNAL, **58**, 857 (1936).

(5) Cohn, *ibid.*, **52**, 3685 (1930).

PROPERTIES AND ANALYTICAL DATA

Compound	Solvent	M. p., (corr.) °C.	Formula	Carbon, %		Hydrogen, %			%	
				Calcd.	Found	Calcd.	Found		Calcd.	Found
Oxime of 2-acetylphenanthrene[a]	EtOH	196–198	$C_{16}H_{13}ON$					N	5.95	5.93
3-(Methylamino)-phenanthrene[b]	Pet. ether (70–90°)	69–70	$C_{15}H_{13}N$	86.91	86.97	6.32	6.33			
Hydrochloride	EtOH-ether	190–200 dec.	$C_{15}H_{14}NCl$					Cl	14.55	14.63
3-(Dimethylamino)-phenanthrene[b]	Pet. ether (70–90°)	75–76	$C_{16}H_{15}N$	86.84	86.80	6.83	7.04			
Hydrochloride	EtOH	210–213 dec.	$C_{16}H_{16}NCl$					Cl	13.76	13.96
3-(1-Aminoethyl)-phenanthrene-HCl[c]	EtOH	265–266	$C_{16}H_{16}NCl$	74.52	74.45	6.25	6.40	Cl	13.76	13.59
"Naphthoquinoline"	Bz pet. ether	106–107	$C_{17}H_{11}N$	89.04	89.11	4.84	4.95	N	6.11	6.09
Hydrochloride	EtOH	239–243	$C_{17}H_{12}NCl$					N	5.27	5.17
Tetrahydro-"naphthoquinoline"[d]	EtOH	72–74	$C_{17}H_{15}N$	87.51	87.78	6.49	6.63	N	6.01	6.16
Hydrochloride	EtOH	255–260	$C_{17}H_{16}NCl$					N	5.19	5.19
Octahydro-"naphthoquinoline"[d]	Pet. ether	111–112	$C_{17}H_{19}N$	86.02	86.04 86.14	8.07	8.16 8.20	N	5.91	5.95
Hydrochloride	EtOH	305–307	$C_{17}H_{20}NCl$					N	5.12	5.15
2-(3-(Dimethylamino)-1-chloro-*n*-propyl)-phenanthrene hydrochloride[e]	EtOH	248–252 dec.	$C_{19}H_{21}NCl_2$					Cl	21.22	20.57
2-(3-(Dimethylamino)-*n*-propyl)-phenanthrene hydrochloride[f]	EtOH	222–227	$C_{19}H_{22}NCl$	76.07	76.01	7.41	7.25	Cl N	11.83 4.67	11.79 4.59

[a] Five grams of finely divided 2-acetylphenanthrene (m. p. 143–144°), 4 g. of hydroxylamine hydrochloride, 80 cc. of alcohol and 2 cc. of pyridine were heated in a pressure bottle for three and one-half hours at 100°. Practically pure oxime crystallized from the cooled reaction mixture; yield, 90%.

[b] The methylation of 3-aminophenanthrene was carried out in 10-g. batches using dimethyl sulfate and potassium hydroxide. The separation of the tertiary and secondary bases was effected by Hinsberg's method with benzene sulfonyl chloride. The quaternary compound was isolated as the methiodide. This, on thermal decomposition, yielded another batch of tertiary amine. The average yield of tertiary amine was 40–50%, of secondary amine, 10%.

[c] Obtained in yields of 60–70% by reduction of the oxime with 2.5% sodium amalgam in alcohol–acetic acid solution.

[d] Ten grams of "naphthoquinoline" suspended in 15 cc. of absolute alcohol with 1 g. of Chromite catalyst was heated to 135° during one hour, and kept at this temperature for one and one-half hours under a hydrogen pressure of 133–144 atm. (apparatus, Adkins and Cramer, THIS JOURNAL, **52**, 4349 (1930), catalyst, 37 KAF, *ibid.*, **54**, 1138 (1932)). The catalyst, together with the crystallized reduction product was filtered, the base (7.5 g., m. p. 70–74°) was separated from the catalyst by extraction with ether in a Soxhlet apparatus. From the alcoholic filtrate 1.5 g. of tetrahydronaphthoquinoline hydrochloride was obtained. No other substances could be obtained. Five grams of naphthoquinoline, dissolved in 125 cc. of glacial acetic acid, was reduced catalytically under ordinary conditions, using 0.25 g. of platinum oxide. Within ten days 1700 cc. of hydrogen was taken up (calcd. for 2 moles, 1100). Three and one-half grams of the octahydro compound was obtained by the aid of its difficultly soluble hydrochloride. When the hydrogenation was interrupted after about two and a quarter moles of hydrogen had been taken up, octahydro- and tetrahydronaphthoquinoline and a considerable amount of oily, undefined products were obtained. The octahydronaphthoquinoline may be prepared more conveniently by catalytic reduction (platinum oxide and glacial acetic acid) of the tetrahydro compound. The tetrahydronaphthoquinoline is rather unstable and becomes dark in solution.

[e] To a suspension of 1 g. of phosphorus pentachloride in 2 cc. of chloroform, 1 g. of finely powdered 2-(3-(dimethylamino)-1-hydroxy-*n*-propyl)-phenanthrene hydrochloride (Mosettig and van de Kamp, unpublished results) was added in small portions, and the mixture was shaken for several minutes. The hydrochloride was precipitated with ether and recrystallized from alcohol; yield, 0.7 g. Its m. p. depends greatly on the speed of heating.

[f] A suspension of 0.075 g. of palladous hydroxide–calcium carbonate catalyst (Pd content 1%), and 0.5 g. of 2-(3-(dimethylamino)-1-chloro-*n*-propyl)-phenanthrene hydrochloride in 10 cc. of alcohol was shaken in a hydrogen atmosphere. The hydrogen absorption was completed in two hours. The catalyst was filtered off, the alcohol was evaporated *in vacuo*, and the residue treated with ether and 10% potassium hydroxide. The brown oily base obtained from the ether layer was distilled in an oil pump vacuum, and converted into the hydrochloride: yield, 30–50%; mol. wt. of free base by micro Rast, calcd. 263; found, 278. In this reduction a white amorphous solid, insoluble in ether and water, was formed, probably according to the equation: $2C_{19}H_{20}NCl \longrightarrow C_{38}H_{40}N_2 + 2HCl$.

a homogeneous liquid which was kept at a gentle boil for nineteen hours. The reaction mixture was steam distilled.

On addition of saturated sodium chloride solution, the naphthoquinoline hydrochloride precipitated in the form of light brown needles. For further purification the base was liberated and taken up in ether. If necessary, a separation from unchanged aminophenanthrene can be effected through the difficultly soluble sulfate of the latter compound. The naphthoquinoline can be purified by high vacuum distillation or by crystallization, and is obtained in the form of long, flat, nearly colorless needles or pale yellow prisms; average yield, 45% of the amount calculated from the aminophenanthrene. The hydrochloride crystallizes in lemon-yellow felt-like needles.

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An Improvement on the Quantitative Determination of Radioactivity

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In an investigation of the mechanism by which acetylchloroaminobenzene rearranges into *p*-chloroacetanilide, which is to be published soon, Olson, Porter, Long and Halford used radioactive chloride ion in order to get one datum in addition to the usual kinetic data. It was necessary to determine the radioactivity of the chloride ion remaining in solution at various times as the reaction progressed. The methods which previously have been used for this purpose have utilized solid materials and because of this have had the following defects in common: (a) lack of reproducibility of the sample due to variations in particle size, crystal structure, thickness of the layer, etc., (b) the activity of the sample is at an optimum for a Geiger counter for a time approximately equal to the half-life of the active material.

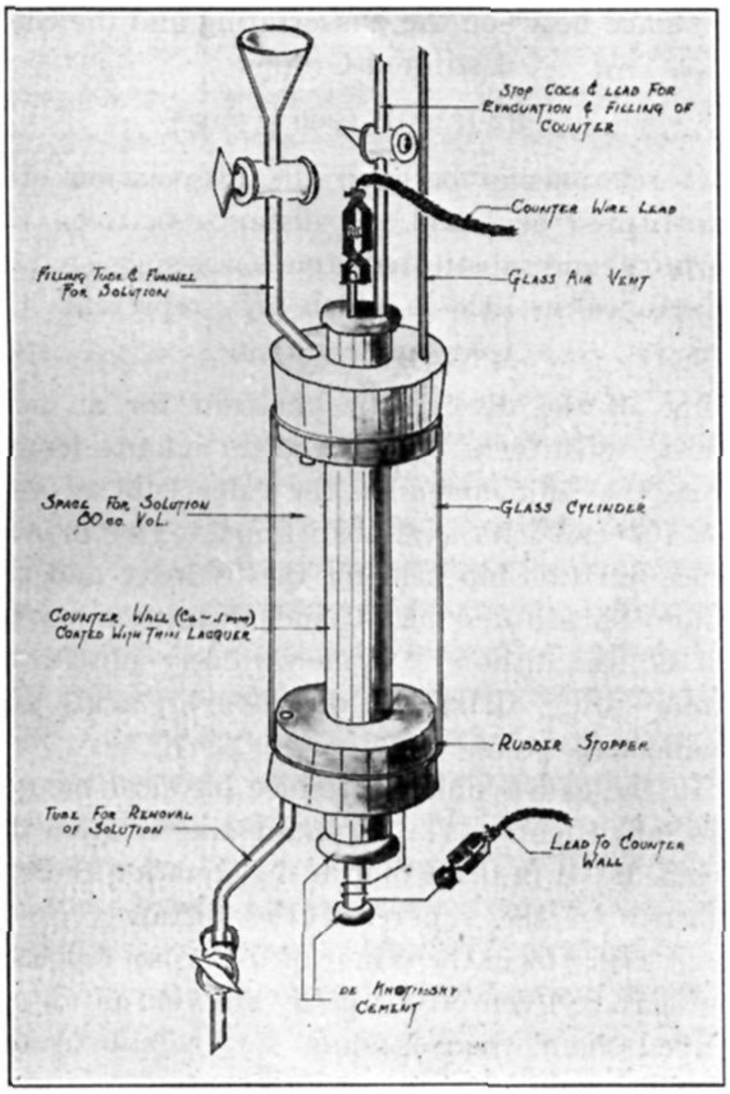

Fig. 1.—Counter assembly for dilution method.

By dissolving the solid material and introducing the solution into a counter of the type shown in Fig. 1, the errors mentioned in (a) can be eliminated. Then, if the original material is sufficiently radioactive, the time during which the counting can be done in the optimum range can be increased many-fold by utilizing a method of dilution of the original solution.

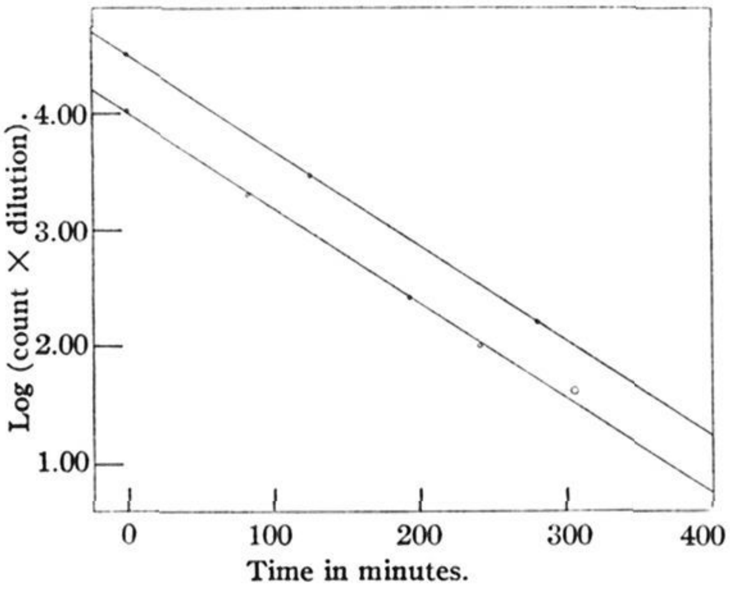

Fig. 2.—Logarithms of the last column of Table I plotted against the time of counting. The circles are these experimental results. The straight lines are calculated under the assumption that the half-life of radioactive chlorine is 37.0 minutes.

Thus in the investigation referred to above, the chloride ion was precipitated as silver chloride, washed and dried. Four-tenth gram of this was dissolved in 15 cc. of five molar ammonium hydroxide and made up to 150 cc. in a volumetric flask with distilled water. This original solution, however, was much too active to be accommodated by the counting apparatus and so 5 cc. of it was used to determine what dilution was necessary to give the optimum counting. The diluent was an ammoniacal solution of silver chloride that differed from the original solution only in