surface. This should be expected if the soot particles, as hexagonal crystals,[6] have grown orientated with their cleavage planes lying parallel to the glass surface.[7]

This view is in agreement with the theory of Eucken, which assumes that the adsorption of gas molecules or atoms by graphite takes place preferentially in the planes perpendicular to the cleavage planes of the crystal lattice.[8] The reaction, therefore, should be facilitated wherever two adjacent crystals touch each other or project into the gas phase.

If this is true, and if the soot deposits are always orientated, the combustion of soot deposits should be accelerated when the underlying glass surface is etched or ground. In order to check this the externally ground part of a Jena glass ground joint and the adjacent smooth surface were coated with soot from a natural gas flame and exposed to oxygen at about 600° for a few seconds. This treatment cleaned the ground part perfectly of carbon, while no visible attack took place on the smooth glass surface, a sharp line dividing the two.

Considering that the deposits in the salt experiments naturally have a very coarse structure, it may be concluded that the function of the salts in the case of soot combustion is quite the same as that of the ground glass, in the above described experiment, namely, interrupting the primary growth of large crystals and preventing a secondary regeneration.

From the same point of view the theory of the mechanism of the steam–carbon reaction should be revised. It is known from the experiments of Frankenburger[9] that sodium chloride inserted into iron deposits causes a highly dispersed structure by inhibiting the growth of coherent crystals. Such iron appears remarkably activated. Accordingly the increased activity of the impregnated graphite seems to be due to the opening of the prismatic planes[6] of the crystal lattice combined with the hygroscopic action of the salt ions.

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[6] U. Hofmann, *Z. angew. Chem.*, **44**, 841 (1931).

[7] The orientation of soot particles is also very probable in its operation as emulsifying agent.

[8] The findings of L. Meyer [*Z. physik. Chem.*, **B17**, 385 (1932)] and U. Hofmann [*Ber.*, **65**, 1821 (1932)] who describe the basal planes of graphite as being attacked preferentially are related to temperatures above 750°.

[9] W. Frankenburger, *Z. Elektrochem.*, **37**, 473 (1931).

Resin Studies. IV. Sublimed *l*-Abietic Acid

BY DAVID LIPKIN AND W. A. LA LANDE, JR.

l-Abietic acid (and rosin) have been observed to give a "sublimate" when heated under a variety of conditions at a temperature below the distillation point of the acid.[1] We have studied this sublimate carefully and find that it shows certain marked differences from the products obtained by Shaw and Sebrell and by Labatut and Duffour. Dupont[2] considered the sublimate obtained by the latter investigators to be identical with *l*-abietic acid.

To obtain a sufficient quantity of the sublimate the previously described procedure of La Lande[1] was used, except that stirring was eliminated and a large glass tube substituted for the reaction vessel. The yield of dry and colorless product was highest in the range 175–275°; at 330–385° the yield was negligible and the product quite impure due to the rapid decomposition. About 0.5 g. of sublimate was collected during an eight-hour period from a 14-g. charge; none was obtained from various rosins, and air or oxygen could not be substituted for the pure nitrogen.

Fig. 1.—"Sublimed" *l*-abietic acid (× 100).

The product, which is illustrated in the accompanying figure, showed the following properties as compared with a sample of *l*-abietic acid prepared according to Steele.[3]

The rotary power of the sublimate was practically constant regardless of the temperature and its rate of formation. It underwent no change on exposure to the light (including occasional sunlight) and air of the laboratory for a few months,

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[1] Labatut and Duffour, *Soc. des Sc. de Bordeaux*, 31 (1919); Shaw and Sebrell, *Ind. Eng. Chem.*, **18**, 612 (1926); La Lande, *ibid.*, **26**, 678 (1934).

[2] Dupont, *Bull. soc. chim.*, [4] **35**, 1209 (1924).

[3] Steele, THIS JOURNAL, **44**, 1333 (1922).

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
$[\alpha]^{25}\text{D}$ (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.

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

JOHN HARRISON LABORATORY
UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA, PA.

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

BY ERICH MOSETTIG AND JOHN W. KRUEGER

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).