TABLE II

Compound		Peimine (P)	Hydrochloride	Hydrobromide	Acid sulfate	Platinchloride	Aurichloride
M. p., °C.		224	295, dec.	293.5–294	278–280	233–235, dec.	164–165
Formula		$C_{26}H_{43}O_3N$	P·HCl	P·HBr	$P·H_2SO_4$	$P_2·H_2PtCl_6$	P·HAuCl₄
Carbon, %	Calcd.	74.75	68.74	62.61	60.53		
	Found[a,b]	74.65[c]	69.07, 68.77	62.92, 62.88, 63.13[a]	60.28, 60.27		
Hydrogen, %	Calcd.	10.38	9.77	8.90	8.80		
	Found[a,b]	10.42[d]	9.84, 9.85	9.04, 8.86, 8.77[a]	8.81, 8.64		
Nitrogen, %	Calcd.	3.35		2.81			
	Found[a,b]	3.56[e]		2.72[a]			
%	Calcd.			Br { 16.04		Pt { 15.68 15.45 15.36	Au { 26.03 24.9 25.09
	Found			15.55[a]			

Molecular weight determination (Rast); 0.288 mg. in 3.520 mg. camphor.

ΔT, 9.2°. 0.268 mg. in 3.810 mg. camphor; ΔT, 7.7°. Calcd. for $C_{26}H_{43}O_3N$, 417.3. Found: 336,[a] 365.[2]

[a] Analyses made by Dr. Ing. A. Schoeller, Toelzestrasse 19, Berlin-Schmargendorf, Germany. [b] Analyses made by Dr. Carl Tiedcke, Bismarckstrasse, Hamburg 19, Germany. [c] Average: 74.75, 74.85,[a] 74.67,[a] 74.76, 74.58,[b] 74.39,[b] 74.53.[b] [d] Average: 10.30, 10.15, 10.49,[a] 10.54,[a] 10.43,[b] 10.53,[b] 10.51.[b] [e] Average: 3.52, 3.60, 3.77, 3.38,[a] 3.36,[a] 3.72.[b]

Summary

Peimine, melting at 224°, has been obtained in a more pure condition. Its formula is $C_{26}H_{43}O_3N$, instead of $C_{19}H_{30}O_2N$, which was assigned to it by Chou. The present formula is substantiated by the results of analysis of several salts; namely, the hydrochloride, bromide, acid sulfate, platinichloride and aurichloride.

SHANGHAI, CHINA　　　　　　　　　　RECEIVED MAY 7, 1936

NOTES

An Apparatus for the Determination of the Absorption of Small Quantities of Gas by Solutions

BY H. E. BENT, W. F. GRESHAM AND N. B. KEEVIL

The apparatus illustrated in the figure is designed to measure the absorption of small amounts of gas by solutions contained in sealed glass capsules. The apparatus allows one to break and empty the capsule, measure the amount of oxygen absorbed and make a correction for the amount of oxygen dissolved in the solvent. The sample is contained in a capsule "G" and the oxygen to be introduced is measured in a capillary by means of the scale "B," a small slug of mercury in the capillary serving to confine the gas.

The particular problem which necessitated the construction of this apparatus was the determination of the purity of small quantities of organic free radicals by measuring the quantity of oxygen absorbed. Samples of a half gram or larger may conveniently be studied in the apparatus developed for measuring the heat of the reaction.[1] Frequently, however, it is desirable to analyze with a precision of about 1% a dilute solution of a free radical which will not absorb more than about 1 cc. of oxygen. The details of breaking the capsule and measuring the absorption of oxygen together with typical experimental results are given in the following paragraphs.

The manipulation of the apparatus will be evident from the figure and the following description. "A" is a stopcock through which the apparatus may be evacuated after the capsule containing the solution of the free radical has been placed in the apparatus. "B" is a scale placed behind the capillary (diameter 4 mm.) in order that the volume of oxygen introduced into the absorption bulb may be accurately measured. "C" is a three-way stopcock which connects the capillary tube to the supply of oxygen and to the

(1) Bent, Cuthbertson, Dorfman and Leary, THIS JOURNAL, 58, 165 (1936); Bent and Cuthbertson, ibid., 58, 170 (1936).

absorption bulb. "D" leads to the oxygen supply and has a blow-off tube below it to permit better control of the pressure. By properly adjusting the pressure a small volume of mercury is introduced into the capillary through "C" before it is filled with oxygen. This slug is blown by oxygen to the top of the capillary. When the cock "C" is carefully turned to introduce oxygen into the absorption bulb which is at a slightly lower pressure the slug of mercury descends and gives a measure of the amount of gas which has been introduced. Provided the tube is clean no difficulty is encountered from the slug's dropping in the capillary. "E" is a thermometer which measures the temperature in the jacket around the absorption bulb. The absorption bulb is just
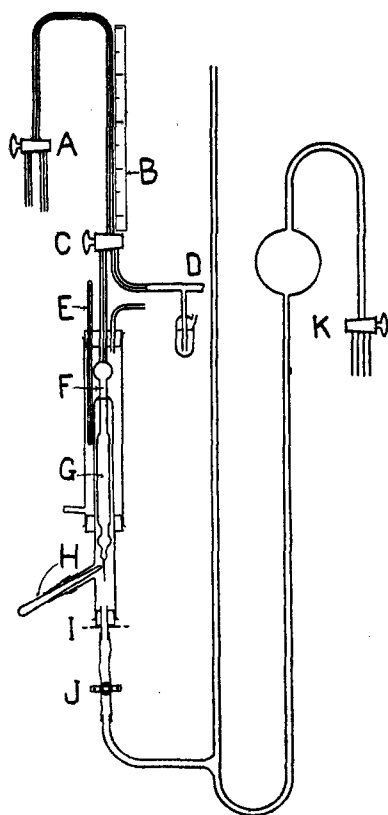

Fig. 1.

above "F" and at "F" is a reference mark to which the bulb is calibrated. "G" is the capsule which is of rather peculiar design. At the top the capsule is sufficiently blunt to prevent its wedging in the constriction. At the bottom there is a little bulge which permits the glass rod "H" to hold the capsule submerged after it has been emptied. The capsule below the lower bulge is constricted for a short length before drawing down

to a capillary. The reason for this is that the capsule cannot easily be emptied unless there is sufficient volume between the lower part of the capsule and the outside tube to hold all of the solution. The contents of the capsule are expelled below the surface of the mercury by warming. If the capsule had not been constricted at the bottom the solution would have come out of the capsule and surrounded the latter, thus making it difficult to expel the contents, as the solution around the outside would have warmed up first and been pushed back into the capsule. The glass rod "H" is connected by a fresh piece of gum rubber tubing. The rubber is connected to a glass tube at such an angle that it is always covered by mercury and does not come in contact with the solution. At the beginning of a run the mercury is lowered and the capsule held by the rod "H." After evacuation the mercury is raised around the capsule and the tip of capsule broken by means of this rod. After emptying the capsule the rod holds the glass down out of the way of the solution while it is absorbing oxygen. "I" is a rubber stopper which is held up by a steel washer which in turn is held securely in place by wires which are not shown. "J" is a pinchcock which permits the mercury to be held at a fixed height in the absorption bulb. "K" is a reservoir of mercury which can be evacuated for removal of mercury from the absorption bulb or may be open to the atmosphere or maintained at any desired intermediate pressure. The pressure in the absorption bulb is measured by means of the mercury column in the tube which is open at the top, a small cathetometer and steel scale, not shown.

In carrying out a run the capsule is first introduced by removing the rubber stopper "I." The pinchcock is closed and the space surrounding the capsule evacuated. Mercury is then allowed to rise, floating the capsule above the rod "H." A correction is made for any trace of residual gas by measuring it before adding the oxygen. The quantity amounted usually to one or two tenths of a cubic centimeter. The pressure is then adjusted, the tip broken and the contents expelled by gentle warming, the broken tip being kept slightly below the surface of the mercury. The pressure is then adjusted to a little less than one atmosphere and an excess of oxygen introduced. The volume of the gas phase is increased to three times that of the calibrated bulb (9.9 cc.), an

auxiliary calibration fixing this point, and the solution allowed to stand with occasional shaking in order to come to equilibrium. The ether meniscus is then raised to the graduation on the constriction at "F" and the amount of residual oxygen computed from the total pressure and the vapor pressure ot the solvent. A correction is applied for the amount of oxygen dissolved in the solvent at the partial pressure of the oxygen existing at the time equilibrium is being established. The compression of the oxygen, as the solution is raised, increases its solubility. However, the surface of contact is so small at the constriction that the new equilibrium is approached very slowly. Since this is a correction to a correction it is not of importance. When ether is used as a solvent the largest error is due to the changing vapor pressure of ether with slight change in temperature. The table illustrates the accuracy which may be obtained without thermostating the water jacket. Doubtless a more accurate control of the temperature by circulating water at constant temperature through the jacket would still further improve the results. The apparatus was checked by determining the solubility of oxygen in ether using a sample of ether about three times as large as that required in the determination of the purity of a free radical. An error of 10% in determining the solubility of oxygen in ether amounts to about 0.5% in the correction to be applied to a run on a free radical. The data on diphenyl α-naphthylmethyl in the table give an idea of the accuracy of the method.

ABSORPTION OF OXYGEN BY DIPHENYL α-NAPHTHYLMETHYL

Concn. of cpd. from soly., wt. %	1.427	1.427
Ether soln., g.	3.074	3.279
O_2 (N. T. P.) added, cc.	2.535	3.065
Inert gas in capsule, cc.	0.165	0.119
Gas after run, cc.	.982	1.275
O_2 abs. by cpd. $\times 10^3$, g.	2.34	2.55
Concn. cpd. in wt. %	1.395	1.426
Purity, %	98.7	100.0

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The Catalytic Oxidation of Carbon

BY HANS M. CASSEL

The activating effect of sodium chloride on the combustion of soot in contact with it, described

by R. K. Taylor,[1] has recently been the object of further interesting experiments by Day, Robey and Dauben,[2] using other salts as activating substances. In explaining their observations these authors refer to a theory proposed by H. S. Taylor and H. A. Neville[3] for the heterogeneous reaction of steam with carbon.

It should be taken into consideration, however, that the topochemical relations in the two cases are distinctly different: in the steam experiments the salt particles are imbedded in the carbon surface; in the combustion experiments, on the other hand, the oxygen molecules have to penetrate the soot layer before they can possibly reach the salt surface.[4] It is difficult to see how the contact of the soot with the salt is maintained and continues to be effective once the reaction has started in the interface.

On the basis of the earlier work of Eucken[5] two observations made by me may offer a more satisfactory explanation. Eucken, studying the combustion of graphite under low pressures, observed a rather low rate on smooth surfaces. But after a longer attack by oxygen the carbon surface takes on a velvet-like appearance, accompanied by an acceleration of the reaction. The condition of the surface may, however, be "ironed out" again by a process which Eucken calls "healing." Probably this is due to the reaction $2CO = C + CO_2$ which takes place in the range of not too high temperatures, the formation of CO being the first step of oxidation. According to R. K. Taylor, this process of regeneration seems to occur also in the case of burning soot, for he observed a slowing down of the reaction "presumably because of the more rapid oxidation at first of smaller particles or more active patches on the carbon surface."

I deposited a layer of soot on Pyrex glass by cracking CH_2Cl_2 at about 450°. In burning this by exposing it to a current of oxygen at about 600° the reaction once started generally spreads parallel to the surface, the soot being removed as if swept out by a piston. The fact that the reaction does not visibly proceed perpendicularly to the surface indicates that the carbon deposit is more easily attacked from the sides than from the

(1) R. K. Taylor, THIS JOURNAL, **52**, 3025 (1930).
(2) J. E. Day, R. F. Robey and H. J. Dauben, *ibid.*, **57**, 2725 (1935).
(3) H. S. Taylor and H. A. Neville, *ibid.*, **43**, 2055 (1921).
(4) The impermeability of thin layers of soot is evident in the case where it acts as an emulsifier.
(5) A. Eucken, Z. angew. Chem., **43**, 986 (1930).

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.

(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,

(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).

	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.

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

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PHILADELPHIA, PA.　　RECEIVED APRIL 15, 1936

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]

(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).

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

(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, % Calcd.	Found	Hydrogen, % 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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UNIVERSITY, VIRGINIA   RECEIVED JUNE 1, 1936

An Improvement on the Quantitative Determination of Radioactivity

BY A. R. OLSON, W. F. LIBBY, F. A. LONG AND R. S. HALFORD

In an investigation of the mechanism by which acetylchloroaminobenzene rearranges into p-chloroacetanilide, which is to be published soon, Olson,

Fig. 1.—Counter assembly for dilution method.

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.

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.
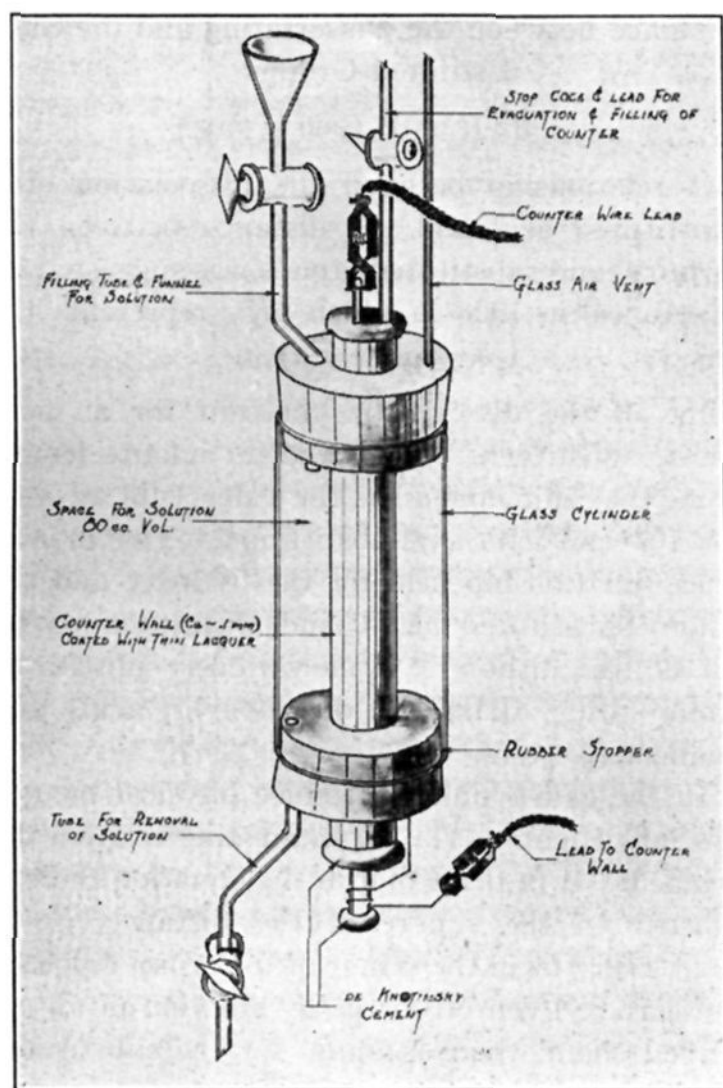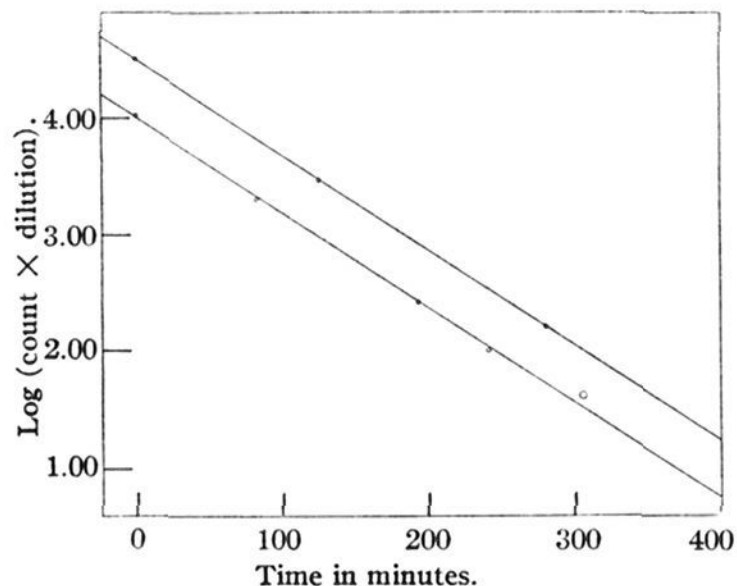

Fig. 2.—Logarithms of the last column of Table I plotted against the time of counting. The circles are these experimental results. The straight lines are calculated under the assumption that the half-life of radioactive chlorine is 37.0 minutes.

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

that the silver chloride was non-radioactive. From this preliminary experiment and the half-life of radioactive chlorine, it was possible to calculate the most advantageous dilution for any subsequent time. With the strength of the sample of radioactive chlorine that was available to us, it was possible to remain in the optimum counting range for six hours even though the first count was not made until two hours after irradiation of the sample.

In Table I and Fig. 2 we show the data for typical determinations.

TABLE I

Results from two experiments. For both, the solutions were 0.0187 molar silver chloride and 0.5 molar ammonium hydroxide. Each count is the result of a ten minute period of counting.

Sample	Time. min.	Dil.	Net count per minute	Net count times the dil.
1a	0	200	158.8 ± 4.5	31760 ± 900
1b	125	20	147.2 ± 4.4	2944 ± 88
1c	280.5	2	81.2 ± 3.6	162.4 ± 7.2
2a	0	80	134.0 ± 4.0	10520 ± 320
2b	82	20	101.3 ± 3.7	2026 ± 74
2c	193	2	134.0 ± 4.0	268.0 ± 8
2	241	1	102.5 ± 3.7	102.5 ± 3.7
2	305.5	1	41.9 ± 2.8	41.9 ± 2.8

The use of this method for any material that can be brought into solution is obvious. It may be worthwhile to point out that the diluent should be chemically identical with the stock radioactive solution in order to eliminate any errors due to differential absorption.

CHEMICAL LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIF.   RECEIVED MAY 18, 1936

5,7-Diiodo-8-hydroxyquinoline

BY VIKTOR PAPESCH AND ROBERT R. BURTNER

5,7-Diiodo-8-hydroxyquinoline, which is of therapeutic interest, has been prepared previously by the interaction of iodine and sodium iodide with 8-hydroxyquinoline in alkaline solution.[1] Although the yield is satisfactory, the procedure requires working in rather dilute solution, thus involving the use of large-scale equipment even for semi-commercial production. A different procedure was therefore developed which is distinctly more economical with respect to ease of manipulation and materials required.

A solution of 2105 g. (14.5 moles) of 8-hydroxyquinoline in 5800 cc. of 15% (by weight) hydrochloric acid is added in a slow stream with stirring

(1) British Patent 351,605.

at laboratory temperature to 4872 g. (30.0 moles) of iodine monochloride dissolved in 6000 cc. of 15% hydrochloric acid. Stirring is continued for four hours longer and the mixture then allowed to stand for twelve hours. The product is washed by decantation with 5% hydrochloric acid to remove excess iodine monochloride, followed by a washing with water and finally with a 2% solution of sodium hydrosulfite to reduce traces of free iodine. An additional amount of product may be recovered by combining the liquors of the first two washings and allowing them to stand for several days. The total yield of product melting at 198—200° is 4900–5300 g. or 83.5–92.5% of the theoretical, the purity of which is approximately 98.5% as determined by iodine analysis.

RESEARCH LABORATORY
G. D. SEARLE & CO.
CHICAGO, ILLINOIS   RECEIVED APRIL 23, 1936

On a Relation between the Dissociation Constants of Substituted Aliphatic Acids and the Distance between the Dissociating and the Substituted Groups

BY JESSE P. GREENSTEIN

A relationship between the dissociation of a substituted acid and the distance between the carboxyl and substituted groups was suggested by MacInnes[1] in 1928 in which pK_∞ represents the

$$pK = pK_\infty + S(1/d) \tag{1}$$

value of the dissociation constant for an acid whose substituent is removed an infinite length along the chain, and d has the value 1 for an α-, 2 for a β- and 3 for a γ-substitution. This inverse linear relationship held for the hydroxy and the chloro substituted acids, and was extended by subsequent authors[2-4] to the variously substituted amino acids, diamines, dicarboxylic acids and amino acid esters.

In the endeavor to introduce physical quantities into equation (1), an interesting relation developed. If in place of d in the equation there is substituted the square of the distance, l^2, in Ångströms, from the center of the group dipole to the carboxyl center on the assumption of an extended chain, there is found for the substituted aliphatic acids an inverse linear relationship between pK and l^2.

(1) MacInnes, THIS JOURNAL, 50, 2587 (1928).
(2) Edsall and Blanchard, ibid., 55, 2337 (1933).
(3) Greenstein, J. Biol. Chem., 96, 499 (1932).
(4) Schmidt, Appleman and Kirk, ibid., 81, 723 (1929).

In applying this consideration to substituted aliphatic acids, we may assume tetrahedral symmetry for the carbon atoms, and the estimates of Pauling and Sherman[5] that the interatomic distance from the carboxyl carbon to the two oxygens is 1.29 Å. and the bond angle 124°. The linear component of the carboxyl group will be, therefore, 0.6 Å. In the case of the amino and hydroxyl substituents the mid-point of the dipole may be located in the center of the nitrogen and oxygen atoms, respectively. On the other hand, for the halogen substituents the dipole will lie somewhere along the halogen–carbon bond and we may for all purposes designate its center as midway along this bond. Using the value of the half tetrahedral angle and Pauling's single bond distances,[6] and expressing the straight line distance l from the dipole center to the carboxyl center in terms of Ångströms, there is found for the variously substituted molecules the following data for l^2:

TABLE I

Position	OH l^2	NH$_2$ l^2	Cl l^2	Br l^2	I l^2	COOH l^2
α	9.18	9.36	6.66	6.97	7.34	13.84
β	18.40	18.66	14.75	15.21	15.76	24.80
γ	30.80	31.14	26.01	26.63	27.35	38.94
δ		46.79	40.45	41.22	42.12	56.25
ϵ		65.61				76.74
ζ						100.4
η						127.2
θ						157.8

(Substituted groups)

Substitution of the above values in the formulation

$$pK = pK_\infty + S(1/l^2) \qquad (2)$$

leads to an excellent linear agreement between pK and $1/l^2$ (Fig. 1), where the values of pK have been derived from Cohn[7] and from Simms.[8]

Examination of the values in Table I suggests the linear integer relation of MacInnes, l^2 for a β-substitution appears to be about twice that for the α-substitution, for a γ-substitution l^2 is about three times that for the α-value, etc. Similar to MacInnes' findings, the lines for the chloro, bromo and iodo acids are identical. Furthermore, within the limits of accuracy of this type of calculation the pK_∞ values derived from either equation (1) or (2) are identical. For the dicarboxylic acids only the value for malonic acid, where both carboxyls are attached to the α-

(5) Pauling and Sherman, *Proc. Nat. Acad. Sci.*, **20**, 340 (1934).

(6) Pauling, *ibid.*, **18**, 293 (1932).

(7) Cohn, *Ergebnisse Physiol.*, **33**, 781 (1931).

(8) Simms, THIS JOURNAL, **48**, 1251 (1926).

carbon falls widely off the curve and has been omitted from the graph. The inability to fit this acid into any relation involving its higher isomers has been discussed by Gane and Ingold.[9]
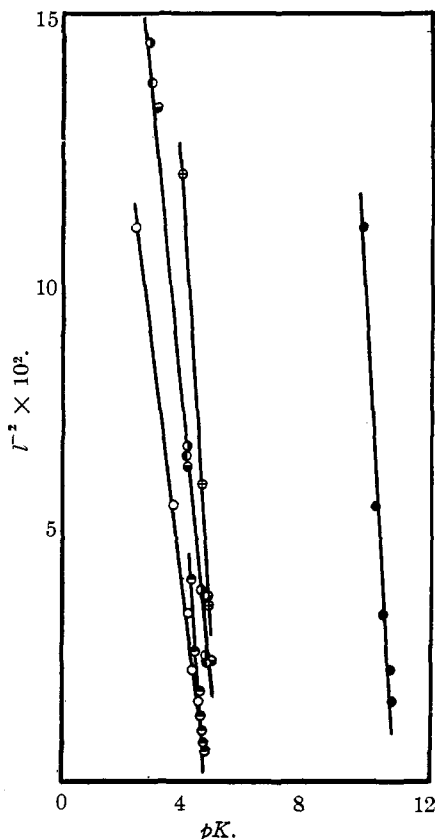

Fig. 1.—Amino acids, pK_1 ○, pK_2 ●; hydroxy acids, ⊕; chloro acids, ◑; bromo acids, ◐; iodo acids, ◓; dicarboxylic acids, ◒.

The constants in equation (2) for the variously substituted acids are gathered in Table II.[10]

TABLE II

Substituent	Ionizing group	pK_∞	$-S$
OH	COOH	5.2	0.085
COOH	COOH	4.7	.081
COOH	NH$_2$	10.9	.089
Halogens	COOH	5.1	.067
NH$_2$	COOH	4.8	.040

Equation (2) recalls the formulation of the field due to a dipole at a distance from its center large in comparison to the distance of separation of the two charges: $V = (\mu/d_0^2) \cos \theta$, where μ is the

(9) Gane and Ingold. *J. Chem. Soc.*. 1594 (1928).

(10) If the interatomic zigzag distance in Ångströms through the chain from the center of the substituent to the center of one of the oxygens of the carboxyl group be considered, an analogous inverse square relation between dissociation constant and distance is revealed in all the cases discussed above. Only malonic acid again provides an exception.

electric moment and θ the angle between d_0 and the dipole axis. It would be difficult, in view of the changes in orientation of the dipole along the chain to derive at present any closer basis of relation other than analogy between the two formulations. It is interesting to note, however, that the value for the slope constant S in equation (2) is practically identical for the three halogen acids. The electric moments of the C–halogen bond for the three halogens are likewise very nearly equal. The relative magnitude of the slope constants, however, bears no obvious relation to that of the electric moments of the substituents.

DEPARTMENT OF PHYSICAL CHEMISTRY
HARVARD MEDICAL SCHOOL,
BOSTON, MASS.   RECEIVED MARCH 16, 1936

The Mechanism of the Diene Synthesis

BY EDWIN R. LITTMANN

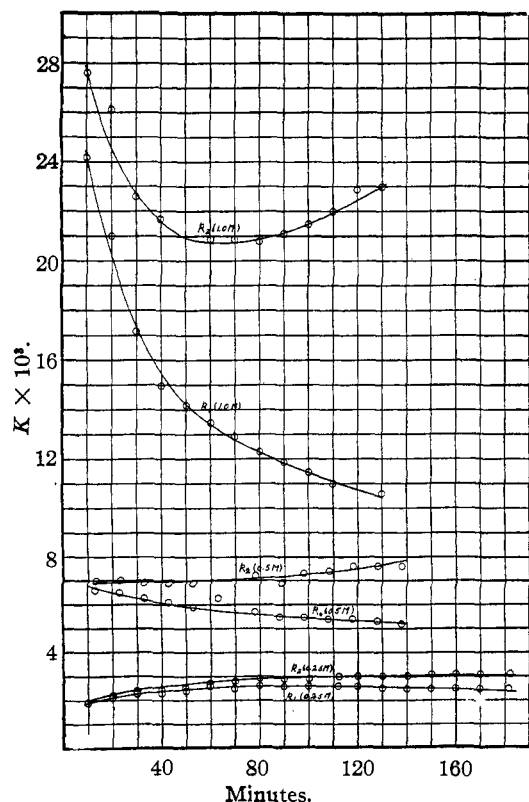The observation of Diels and Alder[1] that a yellow color appears during the synthesis of the

Fig. 1.—Reaction rate constants of α-phellandrene–maleic anhydride.

(1) Diels and Alder, *Ann.*, **460**, 98 (1927).

colorless α-phellandrene-maleic anhydride suggests that the reaction mechanism involves a colored intermediate compound. Such a mechanism would imply a second order followed by a first order process, and in the absence of side reactions the observed reaction rate constants should approach those for a first order reaction as the concentration increases.

To test this matter measurements of the rate of reaction between α-phellandrene and maleic anhydride in acetone solutions have now been carried out at 0.25, 0.50 and 1.0 molality.

The α-phellandrene (Schimmel and Company) had the following properties: specific rotation (sodium light), $-110.7°$; refractive index (white light), 1.4775, and density, both at 20°, 0.856. The maleic anhydride (Eastman Kodak Company) was completely soluble in benzene and was used without further purification. The solutions, cooled to 25°, after thoroughly mixing were transferred to 2-dm. polarimeter tubes and observations of the rotation taken at definite intervals. The temperature of the polarimeter tube was maintained at $25 \pm 0.5°$ by means of an air jet directed on the tube.

The results obtained are given in Fig. 1 in which the rate constants were calculated from the integrated forms of the standard rate equations. The values of the computed constants indicate that the reaction is more nearly unimolecular in the dilute than in the concentrated solutions and therefore it appears either that some other reaction mechanism is involved or that side reactions take place.

In order if possible to isolate the hypothetical polymer formed in the reaction, 6.8 g. of α-phellandrene and 4.9 g. of maleic anhydride were mixed without the use of any solvent and heated to 55–65° whereupon a violent reaction ensued which subsided in a few minutes. After standing for fifteen minutes the mixture was distilled at 3–5 mm. from an oil-bath at 250° until no more distillate was formed. The non-volatile residue was extracted repeatedly with ether, but only a small portion dissolved. The residual white powder when washed with methanol and dried gave, on analysis, 68.7% carbon and 7.27% hydrogen. Its molecular weight by the Rast method was found to be approximately 1220. These data agree with an empirical formula approximating either $C_{46}H_{56}O_{12}$ or $C_{60}H_{74}O_{15}$, giving 69.0 or 69.6% carbon, 7.00 or 7.17% hydrogen, and a molecular weight of 800 or 1034, respectively.

Since α-phellandrene and maleic anhydride were the only substances present, and since the

analysis precluded either terpene or maleic anhydride polymers, it seemed highly probable that a polymeric addition product had been obtained in which the average ratio of maleic anhydride to terpene was 4:3 or 5:4. Polymers of probable similar type have been reported by Wagner-Jauregg.[2]

The size of the polymeric α-phellandrene-maleic anhydride molecule and probable excess of anhydride over terpene would seem to exclude any but linear type polymers and would indicate a bifunctional character of the intermediate. An intermediate of the type

(2) Wagner-Jauregg. *Ber.*, **63**, 3213 (1930).
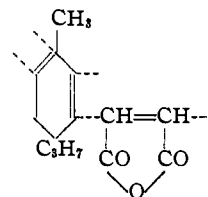
would satisfy the requirements of both polyfunctionality and color and would explain the formation of a polymeric material of the type $C_4H_2O_3$ $(C_{10}H_{16} - C_4H_2O_3 -) C_4H_2O_3$ in which there is an alternation of terpene and maleic anhydride molecules.

HERCULES POWDER CO.
WILMINGTON, DELAWARE RECEIVED DECEMBER 10, 1935

COMMUNICATION TO THE EDITOR

THE DECOMPOSITION OF GASEOUS PARAFFINS INDUCED BY ETHYLENE OXIDE

Sir:

Heckert and Mack [THIS JOURNAL, **51**, 2706 (1929)] obtained evidence that *n*-butane and *n*-pentane were "cracked" in presence of decomposing ethylene oxide at temperatures (—400°) at which the normal rate of decomposition of these paraffins is negligible. We have confirmed this observation in the case of *n*-butane, and have in addition shown that isobutane and propane, but not ethane, also undergo appreciable decomposition under like conditions.

Our method consisted in analyzing the gases, pumped from the reaction vessel, for carbon monoxide (acid Cu_2Cl_2) and for total olefins (bromine water). At a total pressure of about 500 mm. and a temperature of 425°, the following results were obtained.

It will be noted that the relative amount of olefin increases with the complexity of the paraffin; and also (in the case of *n*-butane at least) with the relative amount of paraffin initially present. Since the C_nH_{2n}/CO ratio can exceed unity,

HC.	Initial ratio HC./C_2H_4O	Ratio C_nH_{2n}/CO by anal.
C_2H_6	1.6	<0.05
C_3H_8	1.6	.55
i-C_4H_{10}	1.7	.75
n-C_4H_{10}	1.6	1.2
n-C_4H_{10}	4.1	4.5
n-C_4H_{10}	8.0	12.

it is evident that reaction chains may be set off in the paraffin.

The rate of pressure increase falls off rapidly as reaction proceeds, which may indicate that the products of the paraffin decomposition are inhibiting reaction. A similar result is obtained in the uninduced decomposition of paraffins [e. g., Pease and Durgan, *ibid.*, **52**, 1262 (1930)].

The effect of temperature on the C_nH_{2n}:CO ratio is not great.

The accelerated decomposition of acetaldehyde in presence of ethylene oxide noted by Fletcher [*ibid.*, **58**, 534 (1936)] has been confirmed.

This work is being continued.

PRINCETON UNIVERSITY   L. S. ECHOLS, JR.
PRINCETON, N. J.   R. N. PEASE
              RECEIVED JUNE 24, 1936