1-Phenanthroic Acid.—1-Phenanthroic-acid-anilide hydrolyzes with difficulty; it is practically unaffected by a boiling alcoholic solution of hydrochloric acid or potassium hydroxide. Small amounts can be hydrolyzed readily in a sealed tube. A mixture of 2.0 g. of the product which was obtained by rearrangement of the oximes (containing 82% of 1-phenanthroic-acid-anilide), 10 cc. of concentrated hydrochloric acid and 50 cc. of glacial acetic acid was heated in a sealed tube at 200° for eight hours. The liquids were evaporated and the residue was digested with hot water in order to remove the 1-aminophenanthrene (0.17 g.). The 1-phenanthroic acid which remained was purified through its ammonium salt; yield 0.95 g. (77%).

For making larger amounts of 1-phenanthroic acid it was found more practical to carry out the following reactions: $C_{14}H_9CONHC_6H_5 \longrightarrow C_{14}H_9C(Cl)=NC_6H_5 \longrightarrow C_{14}H_9COOH$. The imide chloride prepared from 20 g. of the rearrangement products as described above was added to a solution of sodium methylate which had been prepared from 5 g. of metallic sodium, 20 cc. of methyl alcohol and 20 cc. of ether. After the mixture had been refluxed for an hour, the solvents were distilled off, and the inorganic material was removed by extraction with water. The methoxyl derivatives of the imides were then hydrolyzed by heating them with a mixture of 50 cc. of concentrated hydrochloric acid and 200 cc. of methyl alcohol for two days. After removal of the solvents, the residue was heated with 100 cc. of a 25% solution of potassium hydroxide in methyl alcohol for twelve hours in order to hydrolyze the methyl ester of 1-phenanthroic acid which had formed in the preceding treatment. The solvent was removed, and the potassium salt of 1-phenanthroic acid was extracted from the residue by 1 liter of boiling water; yield of 1-phenanthroic acid, 7.2 g. From the undissolved residue 2.45 g. of 1-aminophenanthrene was extracted by hot dilute hydrochloric acid. The remainder of the product was unchanged 1-phenanthroic-acid-anilide which could be used over again.

Summary

The orientation of the 1-, 2-, 3- and 9-phenanthryl groups with respect to the methyl and the phenyl group in the oximes of the acetylphenanthrenes and benzoylphenanthrenes has been determined.

The Beckmann rearrangement has been developed as a practical method for the preparation of 1-, 2-, 3- and 9-aminophenanthrene.

A number of new 1-phenanthrene derivatives have been synthesized.

ANN ARBOR, MICHIGAN RECEIVED AUGUST 17, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND SWARTHMORE COLLEGE]

The Effect of Various Catalysts on the Phenanthrene–Bromine Reaction

BY CHARLES C. PRICE

The reasons for undertaking an investigation of the influence of catalysts on the reaction of phenanthrene with bromine have been presented in a previous paper.[1]

Since dioxane, one of the few available nonpolar solvents unattacked by bromine at room temperature, has been found useless as a solvent for the rate determinations due to its phenanthrene-induced bromination,[1] carbon tetrachloride was used, although it was by no means ideal for the purpose. The slight solubility of hydrogen bromide in this solvent makes it difficult to determine accurately the rate of formation of this product, even when ground-glass-stoppered reaction flasks are used. In a blank test at the maximum concentration of hydrogen bromide of the experiments, the sodium hydroxide titer decreased about 25% in ten hours. The bromine, carbon tetrachloride and phenanthrene were purified as described in the previous paper. The iodine was resublimed.

(1) Price, THIS JOURNAL, **58**, 1834 (1936).

All the rate measurements were made at 25°. Samples of the reaction mixture were pipetted into dilute potassium iodide, the liberated iodine then being titrated with sodium thiosulfate and the acid with carbonate-free sodium hydroxide. The disappearance of the iodine color was taken as the end-point of the first titration while phenolphthalein was the indicator in the second. The thiosulfate titer is a measure of the course of both addition and substitution, while the acid is produced by substitution alone.

The bromination catalysts investigated included aluminum chloride, antimony pentachloride, iodine, phosphorus trichloride, phosphorus pentachloride and stannic chloride. When one-tenth equivalent of catalyst was added to an equimolecular solution of bromine and phenanthrene, all of these compounds, especially iodine, catalyzed the formation of hydrogen bromide in appreciable quantities within an hour or two, although without the catalyst there was none formed after several days. Since iodine gave the

best catalysis, as well as more conveniently and accurately measurable rates, it was employed in a majority of the experiments.

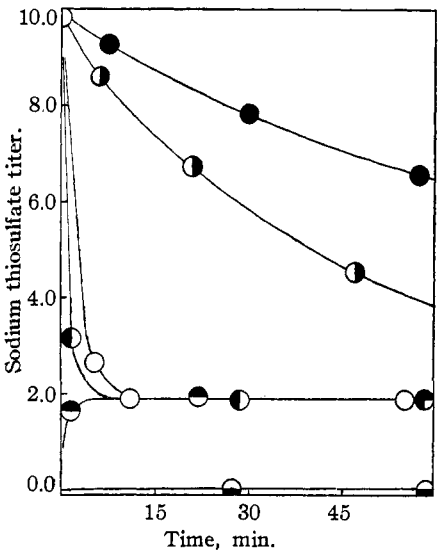


Fig. 1.—Rate of phenanthrene–bromine addition reaction: ○, phenanthrene and pure bromine; ◑, phenanthrene and commercial bromine; ◐, phenanthrene, commercial bromine and antimony pentachloride (10:10:1); ●, phenanthrene, pure bromine and iodine (20:20:1); ◒, phenanthrene dibromide; ◓, phenanthrene dibromide and antimony pentachloride (10:1).

In addition to their effect on the substitution reaction, two of the catalysts had a pronounced effect on the addition, iodine retarding the rate while antimony pentachloride greatly accelerated it. As little as one-twentieth equivalent of iodine in 0.05 *M* phenanthrene and bromine increased the time required to reach the equilibrium of the addition reaction from less than ten minutes to at least three or four hours. With twice as much iodine the rate was practically identical, while with five times as much, or one-fourth the equivalent amount, the rate was slightly greater. The reason for this retardation of the bromination being so little dependent on the iodine concentration may be because, although the rate of the addition reaction is diminished in some fashion proportional to the iodine concentration, the rate of bromine substitution increases so as to become appreciable.

This inhibitory effect of iodine is most probably due to interruption of the chain mechanism for the reaction suggested in the previous paper.[1]

$$C_{14}H_{10} + Br \rightleftharpoons C_{14}H_{10}Br \overset{Br_2}{\rightleftharpoons} C_{14}H_{10}Br_2 + Br$$

The iodine probably reacts with the chain-propagating bromine atoms.

The results of the experiments showing the catalytic effect of antimony pentachloride on the addition reaction are given graphically in Fig. 1. Since the rate of addition of pure bromine to phenanthrene was so rapid as to make it difficult to detect a catalytic effect, commercial "pure" bromine was employed. That the effect of the antimony pentachloride is true catalysis of the addition reaction and not neutralization of the effect of some negative catalyst present was clearly demonstrated by its catalytic effect on the reverse reaction, the attainment of equilibrium by the dissociation of the dibromide. Since antimony pentachloride has frequently been employed as a chlorinating agent, it appears capable of donating a molecule of halogen, perhaps stepwise as atoms, which would initiate the chain reaction for the bromine addition or its reversal.

The results of three measurements of iodine-catalyzed substitution are shown in Fig. 2. In

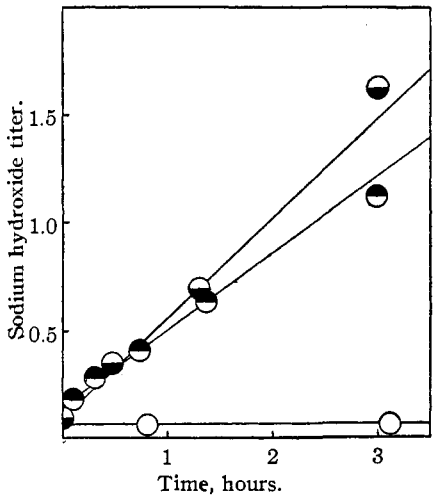


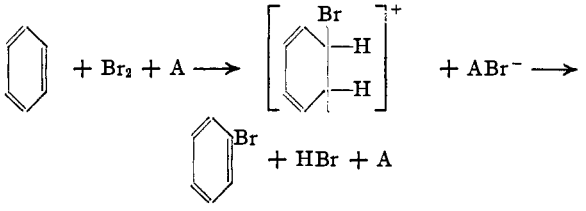
Fig. 2.—Rate of formation of 9-bromophenanthrene: ◓, phenanthrene, bromine and iodine (15:15:1); ○, phenanthrene dibromide and iodine (15:1); ◒, phenanthrene dibromide, bromine and iodine (15:1:1).

one experiment one-fifteenth equivalent of iodine was added to equimolecular quantities of phenanthrene and bromine (*ca.* 0.10 *M*), while in a second the same amount of iodine was added to 0.10 *M* phenanthrene dibromide. A third experiment was identical with the second with the exception of the addition of bromine equivalent to the iodine.

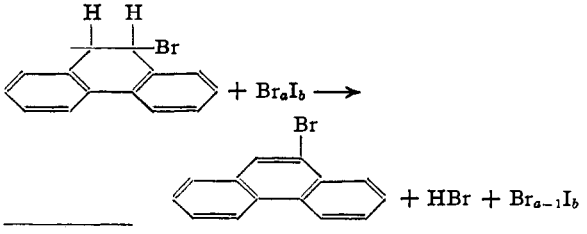
The only way to reconcile the experimental

data with the addition–elimination theory is to suppose that iodine strongly catalyzes the elimination reaction, thus counteracting its inhibitory effect on the addition reaction. The fact that no hydrogen bromide was formed in the second experiment above might then be explained by supposing that the presence of bromine is essential. The identity of the rates in the first and third experiments, however, eliminates the possibility of direct action on phenanthrene dibromide (or phenanthrene) as the mechanism of the production of the hydrogen bromide since in either case the initial rate in one of the two experiments would have been zero. Thus an addition–elimination definitely does not seem to be involved.

Since solutions of phenanthrene dibromide are quite stable and only proceed to equilibrium on the addition of a small amount of bromine, and from the results of the second and third experiments above, it appears that the progress of the addition reaction is necessary to the catalytic effect. These facts, as well as the identity of the rate of hydrogen bromide formation starting with phenanthrene or the dibromide, seem to point to an intermediate radical, perhaps that of the addition reaction, as the molecular species influenced by the catalyst, since this would be present in approximately equal amounts in both experiments. The course of the reaction would then be quite similar to that proposed by Pfeiffer and Wizinger[2] for aromatic substitution. Taking the bromination of benzene as an example, they propose the mechanism



A being a catalyst for the reaction, perhaps a molecule of bromine itself. It seems more likely, at least in the case under investigation, that the intermediate is not a carbonium ion type but a free radical.



(2) Pfeiffer and Wizinger, *Ann.*, **461**, 132 (1928).

Due to lack of completely quantitative accuracy in the experimental method the exact values of the quantities a and b could not be determined. An indication of their probable value, however, can be obtained by a recalculation of experimental work of Bruner,[3] who has presented a detailed account of extensive kinetic measurements of the bromination of benzene with iodine as catalyst. Since excess benzene was used as the solvent, the rates were dependent only on the bromine and iodine concentrations. Bruner calculated rate constants of the second order with respect to bromine but was unable to derive any relation for their dependence on the iodine concentration. However, rate constants of the three-halves order with respect to bromine have been calculated from Bruner's data and found to be equally as good as his second order constants with the additional argument in their favor that the dependence on the iodine concentration now can be determined readily by assuming proportionality to the five-halves power, giving the following expression for the rate of bromination of benzene in benzene as solvent with iodine as catalyst

$$dx/dt = k[Br_2]^{3/2}[I_2]^{5/2}$$

Table I summarizes the results of these calculations with Bruner's second order constants included for comparison. If the substitution is considered to take place in two steps, it would then appear that, either according to the mechanism proposed by Pfeiffer and Wizinger with charged intermediates or with radicals as intermediates, the catalyst molecule is BrI_5. Further experimental work is contemplated to determine the exact kinetics of the reaction with phenanthrene in order to verify the identity of the kinetics for the bromination of benzene and phenanthrene.

TABLE I

RATE CONSTANTS FOR THE IODINE-CATALYZED BROMINATION OF BENZENE FROM BRUNER'S DATA

Table[a]	k_2	$[I_2]$, (M)	$k_{3/2}$, exptl.	$k_{3/2}$, calcd.[b]
1A	9.35	0.214	6.70	(6.70)
1B	2.70	.143	2.41	2.43
1C	1.15	.107	1.19	1.19
1D	0.54	.0856	0.65	0.67
2A	3.10	.144	2.54	2.50
2B	0.67	.0898	0.78	0.77
3A	.25	.0717	.38	.42
4D	1.35	.1002	.97	1.00

[a] Numbered as in Bruner's paper.[3] [b] Calculated from the relation $k_{3/2} = 6.70(0.214/[I_2])^{5/2}$.

(3) Bruner, *Z. physik. Chem.*, **41**, 514 (1902).

Grateful acknowledgment is due Professor Louis F. Fieser for proposing the problem and for advice and criticism.

Summary

The effects of iodine on the phenanthrene-bromine reaction have been determined, and from an analysis of the results it is shown that the observations cannot be reconciled with the addition-elimination theory for aromatic substitutions.

SWARTHMORE, PA. RECEIVED AUGUST 14, 1936

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

High Vacuum Distillation of N-Acyl Amino Acid and Polypeptide Esters

BY SAMUEL GURIN[1]

An observation that certain N-benzenesulfonyl polypeptide esters suffer no apparent decomposition at temperatures appreciably above their melting points, suggested that such substances might be distilled satisfactorily under suitable conditions. Since Fischer's work upon the vacuum distillation of amino acid esters, very little further extension of this technique to N-acyl amino acid esters has been made; apparently no successful distillation of polypeptide derivatives of this type has been reported.

Acetylglycine ethyl ester,[2] as well as carbethoxyglycine and alanine ethyl esters[3] may be distilled easily. Muhlemann[4] attempted to apply this technique to several benzoylated amino acid esters, but observed considerable decomposition at a pressure of 2 mm. Cherbuliez[5] prepared a number of N-acetyl amino acid esters, and successfully distilled them, although considerable racemization accompanied the distillation of optically active compounds of this type.

It was found that butyl esters of benzenesulfonylated amino acids could be distilled without decomposition or racemization at pressures of 10^{-6}–10^{-7} mm. with the aid of a mercury vapor pump of the type described by Copley, Simpson, Tenney and Phipps.[6] In Table I are described the results obtained with a number of such compounds which were prepared in most cases by the method previously described by Gurin and Clarke.[7] Although butyl esters were first prepared in order to obtain greater stability (in contrast to methyl and ethyl esters),[8] this precaution was later found to be unnecessary since corresponding ethyl esters could be equally well distilled. Under these conditions distillation begins, in most cases, at temperatures ranging from 10 to 35° above the melting point. No racemization was observed to take place when optically active derivatives of this type were distilled. Thus, benzenesulfonyl-*l*-leucine butyl ester as well as dibenzenesulfonyl-*l*-tyrosine butyl ester showed no change in rotation after distillation. In Table I are listed the approximate distillation temperature ranges, as well as mixed melting points which were made with original and distilled material. Di-benzenesulfonyl-*d*-lysine butyl ester[9] distils extremely slowly, and at a temperature consid-

TABLE I

Substance	M. p., °C.[a]	Dist. temp.	Mixed m. p., °C.
$PhSO_2$-Glycine butyl ester[b]	26	50–55	25–26
$PhSO_2$-Alanine butyl ester[b]	114	120–125	113.5–114
$PhSO_2$-*l*-Leucine butyl ester[b,c]	51	68–73	50.5–51
$PhSO_2$-Phenylalanine butyl ester	107	120–125	106–107
N-$PhSO_2$-Serine butyl ester	55	70–75	55
$PhSO_2$-Methionine ethyl ester	45	75–80	45
Di-$PhSO_2$-*l*-tyrosine butyl ester	98	150–155	98
Di-$PhSO_2$-*d*-Lysine butyl ester	62	155–160	62
Dibutyl-$PhSO_2$-*d*-glutamate[b]	58–59	80–85	58
Dibutyl-$PhSO_2$-*i*-β-hydroxyglutamate[b]	74	95–100	73–74

[a] All temperatures are corrected. [b] Prepared according to method previously described.[7] [c] After distillation $[\alpha]^{25}D$ −15.9° (1% in ethyl alcohol).

(1) National Research Fellow in Biochemistry.

(2) T. Curtius, *Ber.*, **17**, 1672 (1884).

(3) E. Fischer and E. Otto, *ibid.*, **36**, 2106 (1903); E. Fischer and W. Axhausen, *Ann.*, **340**, 123 (1905).

(4) G. W. Muhlemann, *C. A.*, **22**, 1756 (1928).

(5) E. Cherbuliez and Pl. Plattner, *Helv. Chim. Acta*, **12**, 317 (1929).

(6) Copley, Simpson, Tenney and Phipps, *Rev. Sci. Instruments*, **6**, 265 (1935).

(7) S. Gurin and H. T. Clarke, *J. Biol. Chem.*, **107**, 395 (1934).

(8) E. Abderhalden and S. Suzuki, *Z. physiol. Chem.*, **176**, 101 (1928).

(9) The author wishes to acknowledge his indebtedness to Dr. Hans T. Clarke for furnishing a supply of this material.