

A sample of the molecular compound was dehydrogenated in the presence of 10% palladium-charcoal catalyst at a temperature of 220–310°, affording a 70% yield of 2-methyl-9-phenylanthracene (IV), m.p. 120.5–122°. This material gave no depression of melting point when mixed with an authentic sample.⁵

*Oxidation of the molecular compound: 3-methyl-10-phenyl-10-hydroxyanthrone.*¹⁴ One gram of the molecular compound was dissolved in 3.5 ml. of acetic acid and oxidized by dropwise addition of a water solution containing 1.87 g. of chromic anhydride. After the mixture had been heated on the steam bath for 1.5 hr., it was poured into water and the product which separated was crystallized from ethanol, yield 0.85 g. (75%) of granular crystals, m.p. 192–199°. The analytical sample was obtained as colorless granular crystals, m.p. 197.5–199.5° (lit.¹⁵ 198°).

Anal. Calcd. for C₂₁H₁₆O₂: C, 83.98; H, 5.37. Found: C, 83.70; H, 5.35.

The infrared absorption spectrum showed the characteristic absorptions for hydroxyl and carboxyl at 2.79 and 5.98 μ , respectively.¹⁶

2-Methyl-9-phenyl-9,10-dihydroanthracene. From the mother liquor from which the molecular compound had separated, 0.12 g. of long white needles were obtained, m.p. 87–88°. Once recrystallized from ethanol the fine white needles melted at 89.5–90.5°.

Anal. Calcd. for C₁₂H₁₈: C, 93.29; H, 6.71. Found: C, 93.45; H, 6.72.

Ultraviolet absorption maxima were observed at 250, (262), 267, 271, and 276 m μ .

2,3-Dimethyl-9-phenylanthracene (VI). A solution containing 5 g. of *o*-(3,4-dimethylbenzyl)benzoic acid¹⁷ (V) in dry ether was treated with phenyllithium and worked up as in the preparation of 2-methyl-9-phenylanthracene (IV). Recrystallization of the crude product from ethanol afforded 2.42 g. (41%), m.p. 164–166°. The analytical sample crystallized from ethanol as shiny yellow crystals, m.p. 171.5–172.5°.

Anal. Calcd. for C₂₂H₁₈: C, 93.57; H, 6.43. Found: C, 93.36; H, 6.51.

The ultraviolet absorption spectrum had maxima at 228, 259, (316), 332, 348, and 366 m μ .

10-Phenyl-1,2-benzanthracene (VIII). Starting with 5 g. of *o*-(1-naphthylmethyl)benzoic acid (VII),¹⁸ and following the procedure used in the case of the preparation of the analogs (IV and VI), the benzene solution containing the hydrocarbon fraction from the chromatographic separation was concentrated and the product crystallized by addition of ethanol as light yellow plates, m.p. 182–185°, yield 4.06 g. (58%). A sample recrystallized from benzene-ethanol melted at 184–186° (lit.³ 183–184°) and did not depress the melting point of an authentic sample.¹⁹

The ultraviolet absorption spectrum showed maxima at 222, 259, 271, 281, 291, (300), 320, 335, 351, and 366 m μ . This is in good agreement with the reported values.⁸

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(15) A. Guyot and C. Staehling, *Bull. soc. chim. France*, [3] **33**, 1104 (1905).

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(17) E. de B. Barnett and F. C. Marrison, *Ber.*, **64**, 535 (1931).

(18) L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **59**, 1028 (1937).

(19) We are indebted to Frances Montgomery for preparing this sample, using the method of Vingiello, Borkovec, and Shulman (ref. 8).

A Quantitative Study of the Decomposition of *N*-Bromoacetamide in Chloroform and Ethyl Alcohol

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Reports^{2–4} on the synthesis of *N*-bromoacetamide (NBA) mention its decomposition to form bromine. Also bisacetamide hydrobromide has been reported as a decomposition product⁵ or as a by-product from slow addition reactions of NBA.⁶ The present investigation involves quantitative iodometric analysis and quantitative measurements of hydrogen bromide formation during the decomposition of NBA in chloroform-ethyl alcohol mixtures.

Both the NBA and any bromine formed during decomposition would be expected to react with excess potassium iodide to give triiodide ion. In aqueous acetic acid one mole of NBA has been reported to react with iodide ion to give two equivalents of iodine.⁷ This reaction has now been investigated in water with and without acid present as shown in Table I. With acid present these analytical results show that two equivalents of iodine were formed per mole of NBA while in the absence of acid one equivalent of iodine was formed per mole of NBA. The interaction of the acid with the NBA before the potassium iodide was added caused some loss of oxidizing capacity so that the results were low and relatively unreliable as shown in the second entry of Table I. The best analyses in an acid medium were obtained when the acid was added with the potassium iodide or after the potassium iodide. The average value for the determinations with delayed acid addition was 1.996 ± 0.011 where the precision sets the 95% confidence limits of the average.

These analytical results on NBA are consistent with Equation 1 for the reaction in the absence of acid. When acid was added after this reaction took place further iodine was released according to Equation 2 (see the last two entries of Table I). When acid was added with the potassium iodide the reaction given in Equation 3, which is the sum of Equations 1 and 2, took place. No other equations are consistent with the analytical results in the presence of excess iodide ion. No reaction producing hydrogen ion and iodate ion in the absence of added acid can be considered because the reaction

(1) Present Address: Department of Chemistry, Purdue University, Lafayette, Ind.

(2) A. W. Hofmann, *Ber.*, **15**, 407 (1882).

(3) C. Mauguin, *Ann. chim.*, [8], **22**, 302 (1911).

(4) A. Wohl, *Ber.*, **52**, 51 (1919).

(5) A. Hantzsch and F. E. Dollfus, *Ber.*, **35**, 249 (1902).

(6) R. E. Buckles, *J. Am. Chem. Soc.*, **71**, 1157 (1949).

(7) T. Seliwanow, *Ber.*, **26**, 423 (1893).

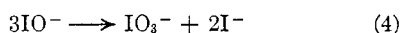
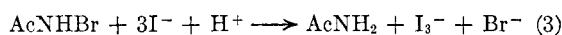
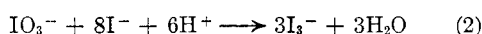
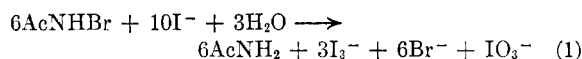
TABLE I

IODOMETRIC DETERMINATION OF *N*-BROMOACETAMIDE (NBA) IN AQUEOUS SOLUTIONS OF VARYING ACIDITY

H ₂ SO ₄ Concn., N	Equiv. Thiosulfate per Mole NBA
0	0.997 ± 0.003 ^{a,b}
0.1–7.0 ^d	1.939 ± 0.058 ^{a,c}
0.5 ^e	1.999
0.5 ^e	1.987
0.05 ^f	2.005
0.05 ^f	1.986
0 ^g	1.005
0.05 ^g	0.996

^a The precision represents the 95% confidence limits of the average. ^b This average represents 9 determinations. ^c This average represents 15 determinations. ^d The acid was allowed to react with the NBA before the potassium iodide was added. ^e The acid was added with the potassium iodide solution. ^f The acid was added after the reaction between potassium iodide and *N*-bromoacetamide had taken place. ^g The acid was added after the first end point was reached with sodium thiosulfate and the mixture was titrated to a second end point.

of Equation 2 would take place and the net result would be Equation 1. Any reaction producing hydroxide ion would lead to the formation of hypiodite ion which would react to give iodate ion by Equation 4 and the sum of the equations would again be Equation 1.



Chloroform solutions of NBA containing varying amounts of ethyl alcohol were analyzed iodometrically as decomposition progressed. No acid was added during the analyses so that each mole of NBA required one equivalent of thiosulfate while each mole of molecular bromine required two. Each mole of bromine must have been formed from two moles of *N*-bromoacetamide, however, so that the titration was a measure of the fraction of the original NBA still unchanged or decomposed to molecular bromine on the basis of one equivalent per mole. The same sample could then be used to determine hydrogen ion concentration as a measure of hydrogen bromide formed as a product of decomposition. This was most conveniently done by the addition of potassium iodate followed by titration with thiosulfate solution. Since NBA reacted so fast with hydrogen bromide to form bromine⁸ it was assumed that no acid would be detected when *N*-bromoacetamide was still present. Representative results of these experiments are given in Table II.

For each mole of NBA the number of equivalents of sodium thiosulfate used plus the number of equivalents of hydrogen ion present should total

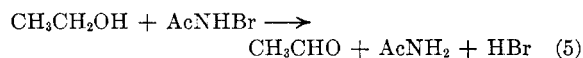
TABLE II

ANALYSIS OF THE DECOMPOSITION PRODUCTS OF *N*-BROMOACETAMIDE IN CHLOROFORM-ETHYL ALCOHOL SOLUTIONS

EtOH Volume Frac- tion	AcNHBr M × 10 ³	Reac- tion Time, Min.	Products, Equiv./Mole NBA		
			Reduc- ible Br	Acid	Total
0.00 ^a	—	—	1.36	0.10	1.46
.00 ^b	—	73	0.88	.00	0.88
.00 ^b	—	105	.60	.00	.60
.00 ^b	—	140	.38	.00	.38
.01	1.72	10	1.04	.00	1.04
.05	1.68	10	0.97	.03	1.00
.05	—	20	.73	.10	0.83
.05	—	45	.46	.28	0.74
.16	1.09	10	.75	.28	1.03
.16	1.57	10	.67	.33	1.00
.25	2.11	10	.78	.18	0.96
.35	1.95	10	.64	.32	.96
.50	2.21	10	.53	.41	.94
.75	0.69	10	.43	.49	.92
1.00	1.80	10	.53	.37	.90

^a This run was carried out until bromine color was deep-est. There was a fairly large air space above the reaction mixture. ^b An effort was made to keep the air space at a minimum in the reaction tubes.

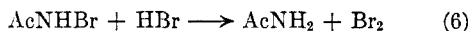
one if the decomposition involved oxidation only. Bromine substitution on the other hand would lead to a total lower than one with a minimum value of zero. When pure chloroform was used as a solvent a slow decomposition to bromine took place and the total of equivalents of reducible bromine and acid was often greater than one. This result was assumed to be caused by air oxidation of the chloroform to phosgene and hydrogen chloride. When the amount of available air was carefully limited no acid was detected and the total of equivalents was considerably less than one as expected for substitution. With ethyl alcohol present the total was never more than one within experimental error. In fact, except when the reaction mixture stood for long enough to allow considerable bromine substitution to take place, the total was very close to one. This fact that nearly all of the bromine from the NBA could be accounted for as either molecular bromine or hydrogen bromide is consistent with the view that the main reaction (Equation 5) was the oxidation of ethyl alcohol to acetaldehyde, which was detected as a product. The oxidations of secondary alcohols⁸ and of aromatic alcohols⁹ by NBA have been reported so that such a reaction with ethyl alcohol is not surprising.



The hydrogen bromide formed would be expected⁸ to react rapidly with NBA as shown in Equation 6. From the type of data given in Table

(8) L. F. Fieser and S. Rajagopalan, *J. Am. Chem. Soc.*, **71**, 3935 (1949).

(9) J. Le Comte and C. Dufour, *Compt. rend.*, **234**, 1887 (1952).



II it was possible to estimate the relative rates of the reactions of Equations 5 and 6. On the assumption that each reaction was first order with respect to each reagent and that any subsequent reactions of bromine would be considerably slower, Equation 7 was derived and was integrated to give Equation 8. The rate constants for Equations 5 and 6 are

$$\frac{dx}{dy} = \frac{Ak_5}{xk_6} - 1 \quad (7)$$

$$x + y = (k_5/k_6)A \ln\left(\frac{A}{A - (k_6/k_5)x}\right) \quad (8)$$

represented by k_5 and k_6 , respectively, while x , y , and A are the concentrations of hydrogen bromide, bromine, and ethyl alcohol (assumed to be constant), respectively. Over the entire range of alcohol concentrations, which were used, the reaction of Equation 6 was found to be $(1.3 \pm 0.3)10^4$ times as fast as that of Equation 5 at room temperature (26°).

EXPERIMENTAL

Pure anhydrous N-bromoacetamide. Crude NBA⁶ was dissolved in a minimum amount of warm water (60°), and the solution was cooled in an ice bath. The crystals were dried thoroughly in an anhydrous atmosphere and then dissolved in cold absolute ether. This solution was chilled and evaporated. The crystals which formed were thoroughly dried at room temperature and then at 45° . A yield of about 50% of NBA, m.p. 108° , was obtained from the purification. The melting point checks well with that of Hofmann² and is considerably higher than those observed (usually around 103°) for products obtained by crystallization from chloroform.^{6,10}

Anal. Calcd. for $\text{C}_2\text{H}_4\text{NOBr}$: C, 17.41; H, 2.92; N, 10.15; Br, 57.93. Found for product of m.p. 108° : C, 17.39; H, 2.89; N (Dumas), 10.21; Br, 57.80. Found for product of m.p. $102\text{--}103^\circ$: C, 16.80; H, 3.11; N, 10.93; Br, 57.30.

Iodometric determination of N-bromoacetamide. A carefully weighed sample of 0.2–0.8 g. of NBA was dissolved in about 25 ml. of water and enough 6N sulfuric acid was added to give a final solution of the desired normality. Potassium iodide (about 3 g.) was then added in enough water to make a total volume of 100 ml. The iodine formed was titrated with standard sodium thiosulfate. The results are tabulated in Table I.

Decomposition of N-bromoacetamide in chloroform and ethyl alcohol. Commercial chloroform was washed free of alcohol by several extractions with concentrated sulfuric acid. The chloroform was washed with water, dried over anhydrous sodium sulfate, and distilled as needed. Samples of 0.1–1.0 g. of NBA were dissolved in 100 ml. of the chloroform, chloroform–ethyl alcohol mixtures, or absolute ethyl alcohol. The solutions were sealed into Pyrex tubes with a minimum of air space and illuminated by a fused silica mercury arc. The tip of each tube was then broken beneath the surface of water. The water solution was first treated with an excess of potassium iodide and titrated with standard sodium thiosulfate solution to determine the amount of reducible bromine present. The solution was then boiled for two minutes, treated with an excess of potassium iodate, and again titrated with standard thiosulfate solution to determine the amount of acid present. The acid was also

(10) E. P. Oliveto and C. Gerold, *Org. Syntheses*, **31**, 17 (1951).

determined in many experiments by titration with standard sodium hydroxide solution following the iodometric titration of bromine. The two methods gave comparable results. Representative data are tabulated in Table II.

Qualitative experiments on the decomposition of N-bromoacetamide. A bromine color rapidly developed when a chloroform solution of NBA with or without ethyl alcohol present was illuminated with ultraviolet radiation. The color reached a maximum intensity, as it was followed by a spectrophotometer, and then the color slowly faded as crystals of bisacetamide hydrobromide precipitated. The melting point varied from 127° to 139° and the material may have been contaminated by monoacetamide hydrobromide or by acetamide. Dry hydrogen bromide reacted with acetamide in chloroform to yield bisacetamide hydrobromide of m.p. $140\text{--}141^\circ$ while the value 139.5° has been reported.¹¹ In other experiments a chloroform-insoluble liquid with the color of bromine was observed partway through the decomposition reaction. Eventually this liquid deposited crystals of bisacetamide hydrobromide and gradually disappeared. It is probable that this liquid was a mixture composed mostly of N-bromoacetamide and acetamide with bromine dissolved in it. In some experiments evaporation of the chloroform solution led to the isolation of small amounts of acetamide. Diacetylhydrazine, m.p., 140° , might be expected as a product, but methods of isolation, which were successful with an authentic sample,¹² did not yield this material from the decomposition solutions.

Detection of acetaldehyde. A solution of 1.4 g. (0.010 mole) of NBA in 20 g. of chloroform and 5 g. of absolute ethanol was stirred rapidly with 2.5 g. of calcium carbonate in diffuse light. Only a very light bromine color was observed. After thirty minutes the solution was filtered and then shaken with water in the presence of a little copper wire. Addition of excess 2,4-dinitrophenylhydrazine solution to the aqueous layer yielded 0.40 g. (18%) of acetaldehyde 2,4-dinitrophenylhydrazone, m.p. $155\text{--}159^\circ$, which after two crystallizations melted at $165\text{--}167^\circ$ and did not depress the melting point of an authentic sample.

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(12) G. Pellizzari, *Gazz. chim. ital.*, **39I**, 536 (1909).

Diels-Alder Reactions on 1,2-Cyclohexenedicarboxylic Anhydride

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1,2-Cyclohexenedicarboxylic anhydride (Δ^1 -tetrahydrophthalic anhydride) has been reported to undergo the Diels-Alder reaction with butadiene^{1,2} to form the octalin derivative, 1,4,4a,5,6,7,8,8a-octahydro-4a,8a-naphthalenedicarboxylic acid. In the present investigation some new octalin derivatives have been prepared by using other dienes with this anhydride. Six dienes were allowed to react with the dienophile in a sealed reaction tube, and adducts were obtained with isoprene and di-

(1) K. Alder and K. H. Backendorf, *Ber.*, **71B**, 2199 (1938).

(2) P. Brigl and R. Herrmann, *Ber.*, **71B**, 2280 (1938).