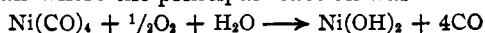


until free hydrochloric acid in 1 *N* concentration is present.

The net result of the use of tartaric acid appears to be the same as that from the use of cysteine and can be represented by the same equation (1). Probably intermediate complexes of a similar nature are formed.

The metering of the carbon monoxide was only approximate. In the first and second runs the excess of CO absorbed over that required by equation (1) is real, it is doubtless due to the formation of some potassium formate. Blanchard and Gilliland⁶ noted the formation of a little nickel formate in the slow oxidation of nickel carbonyl by air where the principal reaction was



Summary

Bromine reacts quantitatively with cobalt nitrosyl carbonyl, displacing nitric oxide and carbon monoxide.

(6) Blanchard and Gilliland, *THIS JOURNAL*, **48**, 872 (1926).

The absorption of carbon monoxide by alkaline cobalt salt solutions is promoted by the presence of cysteine, tartrate and several amino acids as well as the presence of cyanide and sulfide.

Acidification of the KCo(CO)_4 solution obtained by treating alkaline cobalt salt solution containing cysteine or tartrate with carbon monoxide sets free the very volatile hydride HCo(CO)_4 . This hydride can be condensed to a light yellow crystalline solid which melts at -33° to a sulfur yellow liquid and decomposes at room temperature into the non-volatile dimeric cobalt tetracarbonyl and hydrogen. The hydride is distinctly an acid, its acid strength being markedly greater than that of carbonic acid.

Cobalt nitrosyl carbonyl is most advantageously prepared by the use of cysteine as above: after acidification, the hydride is allowed to decompose in the shaking apparatus, then treatment with nitric oxide yields the nitrosyl carbonyl.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Action of Bromine in Methyl Alcoholic Solution on Phenanthrene; a New Route to 9-Phenanthrol and 9-Phenanthrylamines¹

BY L. F. FIESER, R. P. JACOBSEN² AND C. C. PRICE

In connection with a study of the reaction between phenanthrene and bromine in carbon tetrachloride solution,³ a trial was made of the action on the hydrocarbon of a solution of bromine in methyl alcohol. Considering the ready formation of phenanthrene dibromide, and in analogy with known cases of the addition of methyl hypobromite to aliphatic and alicyclic ethylenic linkages,⁴ it seemed possible that the hydrocarbon might add the reagent in a similar fashion.

In the first experiments fine, colorless needles of a reaction product were observed to separate after mixing methyl alcoholic solutions of bromine and phenanthrene at room temperature, but the

(1) The bromination reaction described in this paper was discovered in the course of other work by C. C. Price, who made a preliminary study of the formation of the product and of its conversion to 9-methoxyphenanthrene (Dissertation, 1936). A more detailed investigation of the formation, nature and preparative uses of the compound was subsequently made by R. P. Jacobsen, and these experiments form the basis of the present report.—L. F. F.

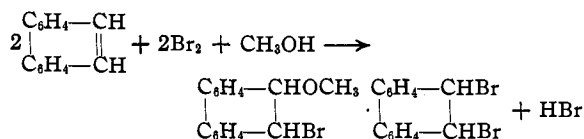
(2) Du Pont Research Fellow.

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

(4) Conant and Jackson, *ibid.*, **46**, 1727 (1924); Jackson, *ibid.*, **48**, 2166 (1926); Jackson and Pasiut, *ibid.*, **49**, 2071 (1927); Meinel, *Ann.*, **510**, 129 (1934).

yield was poor. The results were somewhat improved by working at a lower temperature and by using a large excess of bromine, and it was found that the yield is increased very substantially by carrying out the reaction in the presence of sodium acetate to displace the bromine equilibrium in favor of the hypobromite. Eventually an easily reproducible procedure was developed by means of which a colorless product can be obtained in a quantity amounting to about one and one-third the weight of hydrocarbon employed. This material was granular and possibly different from that first observed. Purified by careful recrystallization, the substance melted at $107.5\text{--}108^\circ$, dec., and when stored in the cold room (5°) it remained apparently unaltered for about one day. At room temperature decomposition set in after a few hours. Although the analysis of the unstable substance presented difficulties, the results for carbon, hydrogen, bromine and methoxyl all point to the formula of a molecular compound composed of equivalent parts of phenanthrene

methoxybromide and phenanthrene dibromide, and the reaction thus appears to proceed as follows.



This formulation is consistent with such observations as have been made of the properties of the substance. When warmed with a solution of potassium hydroxide and potassium acetate in methyl alcohol, it yielded a mixture of about equal parts of 9-methoxyphenanthrene and phenanthrene. The former substance presumably is produced by the elimination of hydrogen bromide from the methoxybromide component, while the latter evidently comes from the dibromide by loss of bromine. When treated in the same way, pure phenanthrene dibromide afforded bromine-free phenanthrene in nearly quantitative yield. While the mixture of the ether and the hydrocarbon is not readily separated, pure 9-phenanthrol can be obtained very easily by short treatment of the crude mixture with hydrobromic-acetic acid followed by extraction with alkali, and the phenanthrene can be recovered in a satisfactory state of purity. Since the most satisfactory of the previous methods of preparing 9-phenanthrol (through phenanthrenequinone and dichlorophenanthrone⁵) leaves much to be desired, the new reaction series was studied with a view to the development of a better source of the hydroxy compound. It was found that all three reactions can be carried out rapidly with reasonably large amounts of material and that 9-phenanthrol can be obtained with regularity in a pure condition in over-all yields of 28-30%, based on the phenanthrene consumed. In its present state the process seems to have definite advantages over previous methods, and it is not impossible that further improvements can be made.

With 9-phenanthrol more readily available, the use of this material as a source of 9-phenanthrylamines was investigated. Such substances are of particular interest because of the structural relationship, in at least one important respect, to morphine. The conversion of 9-phenanthrol into 9-phenanthrylamine is described in the early literature, but the results were unsatisfactory (25%

yield),⁶ and methods of preparing the amine through 9-nitro-,⁷ 9-nitro-10-bromo-,⁸ or 9-acetylphenanthrene⁹ all suffer from the fact that the starting materials are not easily available. Following the general procedure of Bucherer,¹⁰ we obtained the amine from 9-phenanthrol in 90% yield. N-Alkylphenanthrylamines (methyl, ethyl, *n*-propyl and *n*-butyl) were obtained in about 70% yield by heating 9-phenanthrol with the appropriate primary amine and aqueous sodium bisulfite at 135-140° for about one day. N-(β-Hydroxyethyl)-9-phenanthrylamine was prepared from 9-phenanthrylamine and ethylene oxide, but only in poor yield.

The investigation of the bromination reaction is being continued and the preparation of further 9-amino derivatives more closely related to the alkaloids of the morphine group is in prospect.

Experimental Part¹¹

Preparation of the Complex.—After a number of trials at different temperatures and varying the amounts of the reagents, the following procedure was adopted as the most satisfactory both as to yield and quality of the product. For efficient washing of the product, larger amounts are best handled in portions of the size indicated.

A solution of 50 g. of phenanthrene (m. p. 97.5-98°) and 15 g. of anhydrous sodium acetate in 900 cc. of warm methyl alcohol was cooled quickly to about 35-40° without allowing much phenanthrene to crystallize, and a solution of 25 g. of bromine in 100 cc. of cold methyl alcohol was added all at once. The mixture was cooled rapidly in a salt-ice bath and the temperature was brought to -5°. The complex began to separate from the red-brown solution during the cooling process, and after standing at -5° for twenty to thirty minutes the yellow solid was collected and washed, after removing the filtrate, with three 100-cc. portions of a 5% solution of sodium acetate in 70% methyl alcohol. This removed the yellow color and left a nearly white solid. The original filtrate was treated with 75 cc. of 20% aqueous sodium acetate solution and an additional 15-cc. portion of bromine in 50 cc. of cold methyl alcohol, and cooled to -10° for thirty minutes. A second crop of the complex separated, about equal in amount to the first, and it was washed as before. The total product weighed 63-65 g. (71-74%, calculated on the basis of the formula indicated) and melted at 105-107° with loss of hydrogen bromide. This crude product was employed in the next step without purification.

The material prepared in this way did not appear to undergo change when crystallized from ether-petroleum

(6) Japp and Findlay, *J. Chem. Soc.*, **71**, 1115 (1897).

(7) Schmidt and Strobel, *Ber.*, **34**, 1461 (1901); **36**, 2508 (1903); Schmidt and Heinle, *ibid.*, **44**, 1488 (1911).

(8) Schmidt and Lodner, *ibid.*, **37**, 3575 (1904); Austin, *J. Chem. Soc.*, **93**, 1762 (1908).

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

(10) Bucherer, *J. prakt. Chem.*, **69**, 49 (1904).

(11) All melting points are corrected. Analyses by Mrs. G. M. Wellwood.

(5) Lachowicz, *J. prakt. Chem.*, **28**, 168 (1883); Schmidt and Lumpp, *Ber.*, **41**, 4215 (1908); Goldschmidt, Vogt and Bredig, *Ann.*, **448**, 135 (1925).

ether, using Norite for clarifying the solution and avoiding undue heating, and after several recrystallizations it was obtained as a colorless, granular solid, m. p. 107.5–108°, dec. One sample melted at this temperature without showing signs of decomposition. Samples dried in vacuum and kept at room temperature began to turn brown within a few hours, and the sample used for the following analyses was prepared the evening before it was used and stored at 5°. All of the analyses were made on the same sample, but this was recrystallized prior to the second methoxyl determination (the last of the series reported), although no darkening had been observed.

Anal. Calcd. for $C_{14}H_{10}Br_2 \cdot C_{14}H_{10}(OCH_3)Br$: C, 55.51; H, 3.70; Br, 38.24; OCH_3 , 4.95. Found: C, 56.11, 56.23; H, 4.62, 4.97; Br, 38.06, 36.74; OCH_3 , 4.96, 5.49.

The lack of concordance in the results may be connected with the difficulty in drying the sample completely at a low temperature, with its instability, or, particularly in the case of the carbon-hydrogen determinations, with a difficulty inherent in the combustion itself. The bromine content is about 10% higher than that calculated for the pure methoxybromide and this fact, and the definite methoxyl content found, provide convincing indications of the presence of the two components.

One sample, prepared at an earlier stage of the work, crystallized from ether in fine needles, m. p. 113–115°, uncorr., and the carbon value found in a single determination was about 5% higher than found above, but other analyses were not made and it is not known if this was the same or a different product.

In bromination experiments conducted at room temperature in methyl alcohol containing no sodium acetate the yields of the solid product which separated ranged from 20 to 30%. When the solution was cooled to 0° soon after mixing the reagents the yield was increased to 50%.

Debromination.—The crude, undried complex prepared in four lots from 200 g. of phenanthrene was suspended in 1 liter of methyl alcohol containing 40 g. of potassium hydroxide and 10 g. of potassium acetate. The mixture was heated with stirring at 50–55° for one hour, after which the temperature was raised to 60° for thirty minutes. The warm, deep yellow-red solution was decanted from precipitated potassium bromide, the latter being washed with methyl alcohol, and the solutions were combined and diluted with 200 cc. of water and cooled. The oil which separated soon solidified and the material was crystallized from methyl alcohol, using Norite. An additional quantity of material was obtained by further dilution of the mother liquor, and recrystallized. The total yield of material, consisting of a mixture of plates and needles and melting indefinitely at 60–80°, was 110 g. This was found from the subsequent treatment described below to be composed of nearly equal amounts of phenanthrene and 9-methoxyphenanthrene.

In two early experiments by different workers, both using sodium acetate in methyl alcoholic solution, 9-methoxyphenanthrene, m. p. 93–94° (calcd.: C, 86.50; H, 5.76. Found: C, 86.16; H, 5.76) was obtained as the sole product, but the results could not be repeated later. The starting materials were not fully analyzed and may have been different from that described above.

As the formation of phenanthrene from the dibromide

component seemed surprising, a test experiment was made with the phenanthrene dibromide prepared by adding 5 g. of bromine to 5 g. of phenanthrene in 25 cc. of carbon tetrachloride solution and cooling. The crystalline product was washed well and heated for thirty minutes with a solution of 4 g. of potassium hydroxide and 0.5 g. of potassium acetate in 50 cc. of methyl alcohol. On decanting the solution and adding an equal volume of water, 4 g. of halogen-free phenanthrene separated as small leaflets. Once recrystallized it melted at 95.5–97° and gave no depression when mixed with authentic phenanthrene.

9-Phenanthrol.—The crystalline mixture (110 g.) obtained as described above was heated under reflux with 400 cc. of glacial acetic acid, and 60 cc. of 48% hydrobromic acid was added gradually. After boiling the mixture for two hours an equal volume of water was added and the precipitate was collected after cooling, washed, and the moist product was taken up in 300 cc. of ether. After thorough washing with water, the ethereal solution was extracted with three 50-cc. portions of 10% sodium hydroxide and the green alkaline extract, after one washing with ether, was acidified and extracted with 100 cc. of ether. The washed ethereal solution, after dilution with 25 cc. each of benzene and hexane, was dried over sodium sulfate and decolorized by filtration through a column of activated alumina. An impurity giving the solution an orange color was retained in a greenish band, and from the filtrate 48–50 g. of 9-phenanthrol was obtained in the form of faintly salmon-colored needles melting at 153–155°. From the washed ethereal solution remaining after extraction with alkali, 45 g. of crude phenanthrene was recovered, making the over-all yield of 9-phenanthrol 28–30%, based on material consumed. The crude phenanthrene after being distilled in vacuum and crystallized once from methyl alcohol was satisfactory for use in the bromination reaction.

9-Phenanthrylamine.—A mixture of 10 g. of 9-phenanthrol, 50 g. of 40–45% ammonium sulfite, and 50 cc. of concentrated ammonium hydroxide solution was heated in a sealed tube at 135–140° for twenty to twenty-five hours. The cooled mixture was extracted with ether and the solution, after being washed with dilute sodium hydroxide and with water, was dried over sodium sulfate, decolorized with Norite and concentrated somewhat. On adding hexane and cooling, there was obtained 9.1 g. (90%) of 9-phenanthrylamine, m. p. 135–136.8°. One recrystallization from ether-petroleum ether or benzene-hexane gave very faintly yellow needles, m. p. 137.5–138.5°.

In similar experiments conducted at 100° the yield of amine after heating for five hours was 20%, after twenty to twenty-five hours it rose to about 50%.

N-Alkyl-9-phenanthrylamines.—For the preparation of these substances a mixture of 2 g. of 9-phenanthrol, 10 g. of sodium bisulfite and either 10 cc. of water and 10 cc. of a 33% aqueous solution of the amine, or a mixture of 20 cc. of water and 5 cc. of the pure amine, was heated in a sealed tube at 135–140° for twenty to twenty-five hours. The reaction products, recovered as above, were obtained directly in a good condition and the melting point subsequently rose only 1–3° on further recrystallization. The first three substances were crystallized from benzene-ligroin or ether-petroleum ether, while 80% methyl alcohol

was used in the case of the butyl compound. The amines all form heavy, pale yellow needles.

Alkyl group	Yield, %	M. p., °C.	N-ALKYL-9-PHENANTHRYLAMINES			
			% C		% H	
			Calcd.	Found	Calcd.	Found
Methyl	70	88.5-89.5	86.91	86.85	6.33	6.27
Ethyl	70	97-98	86.87	86.96	6.84	7.11
<i>n</i> -Propyl	70	109.5-110.5	86.76	86.61	7.29	7.09
<i>n</i> -Butyl	62	102-103	86.69	86.52	7.69	7.51

N-(β -Hydroxyethyl)-9-phenanthrylamine.—After heating a mixture of 2 g. of 9-phenanthrylamine, 5 cc. of benzene and 10 cc. of ethylene oxide in a sealed tube at 100° for seven hours, the excess ethylene oxide was expelled and the residue was extracted with ether. The solution was dried, decolorized and treated with petroleum ether, when 0.25 g. (10%) of a solid was obtained in the form of fine needles melting at 99.5-101°. The substance has a tendency to separate in a gelatinous condition. After two recrystallizations from ether-petroleum ether it was obtained as long, slender, colorless needles, m. p. 101-102°.

Anal. Calcd. for $C_{16}H_{18}ON$: C, 80.97; H, 6.38. Found: C, 81.22; H, 6.34.

When the reaction mixture was heated at 100° for only five hours considerable 9-phenanthrylamine was recovered along with some of the β -ethanol derivative. On conduct-

ing the reaction at 135-140° for either ten or twenty hours the ethereal extract of the product yielded only a resinous residue on evaporation. This distilled without apparent decomposition at about 250° (2 mm.) but the viscous, pale yellow distillate set to a glass and did not crystallize.

Summary

Treated with bromine in methyl alcoholic solution, phenanthrene is converted in about 70% yield into a very unstable substance which appears to be a complex containing one molecule each of phenanthrene methoxybromide and phenanthrene dibromide. The complex yields 9-methoxyphenanthrene and phenanthrene when warmed with alcoholic potassium hydroxide-acetate, and 9-phenanthrol is easily obtained from the mixture in a sufficiently satisfactory over-all yield to make this a useful preparative method. 9-Phenanthrylamine and typical N-alkyl derivatives can be obtained in good yield from 9-phenanthrol by the Bucherer reaction.

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The Acylation and Alkylation of Beta Diketones and Beta Sulfonyl Ketones

BY E. P. KOHLER AND H. A. POTTER

In a recent paper,¹ in which we described the action of benzoyl chloride on the magnesium derivatives of a series of monoketones, we showed that there is a conspicuous difference in the behavior of phenyl and mesitylenic ketones, the former being converted into diketones and the latter largely into benzoates. We have now extended the comparison to the corresponding β -diketones and, as these diketones form copper derivatives which can be purified by crystallization, we were able to compare the behavior of phenyl and mesitylenic ketones when they are benzoylated by means of metallic derivatives that are very different from the magnesium compounds in their activity.

We also included in the comparison the corresponding β -sulfonyl ketones—tosyl acetophenone and tosyl acetomesitylene. These compounds are of special interest because the sulfonyl group increases the acidity of the hydrogen on an adjoining carbon atom but is incapable of participating in any process akin to enolization.

(1) Kohler, Tishler and Potter, *THIS JOURNAL*, **57**, 2517 (1935).

The nature of the products and the yields in which they were obtained are shown in the following table. In many cases the primary benzoylation products deprived some of the initial metallic derivatives of their metal and thus prevented complete acylation; the proportion of C-benzoyl to O-benzoyl derivatives is therefore more significant than the total yield. In the case of the copper compounds the great differences in solubility introduce an additional complication because in the very slow reactions a part of the initial material is lost through halogenation by the mechanism recently established by Michael and Carlson.² An attempt to obviate this difficulty by substituting benzoyl bromide for the chloride—in the cases marked with an asterisk—was unsuccessful because, while the bromide reacts far more rapidly than the chloride, the resulting cupric bromide is also a much better halogenating agent than the chloride.

An examination of this table shows that the difference in the mode of benzoylation of phenyl

(2) Michael and Carlson, *ibid.*, **58**, 353 (1936).