

As was to be expected^{1,2} compounds in the β -naphthoquinone series possess greater anti-oxygenic activity than the analogous α -naphthoquinones but they are less active than corresponding benzoquinones. Thus, β -lapachone is only about one-fifth as effective as the pyrano-*o*-quinone derived from α -tocopherol. Since β -lapachone is much less effective than α -naphthoquinone, it is doubtful that the chroman ring of the former contributes to its anti-oxygenic action; in the benzene series the presence of a chroman ring markedly increases anti-oxygenic activity.

Obviously, no relation exists between anti-hemorrhagic and anti-oxygenic activity.

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Some Addition Compounds of Morpholine

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During an investigation of dithiane addition compounds of various inorganic substances,¹ it was suggested that morpholine, C_4H_9NO , might form similar complexes. Consequently, several representative addition compounds of zinc, cadmium and mercuric halides have been prepared. These compounds are white, crystalline, soluble in *aqua regia* with decomposition and slowly soluble in water, also with decomposition. In all compounds prepared, there are two moles of morpholine per mole of halide, in contrast to dioxane compounds, reported first by Rheinboldt, Luyken and Schmittmann,² of which only the zinc compounds are analogous, and to dithiane complexes.¹

The addition compounds were prepared by direct reaction between the halide and excess morpholine at the boiling point of the latter. After cooling, the crystals were centrifuged rapidly, washed with absolute alcohol and ether and dried in a vacuum desiccator. In some cases, the inorganic halide was dissolved in absolute alcohol and then added to the morpholine. Addition compounds of morpholine and cupric halides are

(1) Bouknight and Smith, *THIS JOURNAL*, **61**, 28 (1939).

(2) Rheinboldt, Luyken and Schmittmann, *J. prakt. Chem.*, **149**, 30 (1937).

extremely sensitive to moisture, decomposing rapidly. Morpholine also appears to react with cobalt and cupric chloride in hydrochloric acid solution.

The experimental data are summarized in Table I. Zinc and cadmium were determined as anthranilate, mercury as $[Cu(en_2)]HgI_4$.

TABLE I
ADDITION COMPOUNDS OF MORPHOLINE

Formula	M. p., °C.	Metal analyses, %	
		Calcd.	Found
ZnCl ₂ ·2C ₄ H ₉ NO ^a	Softens 200–210, then melts	21.1	21.0
ZnBr ₂ ·2C ₄ H ₉ NO ^a	Dec. 230–240	16.4	16.3
CdCl ₂ ·2C ₄ H ₉ NO ^a	...	31.4	32.2
CdBr ₂ ·2C ₄ H ₉ NO	Dec. 250–252	25.2	24.8
CdI ₂ ·2C ₄ H ₉ NO	Dec. 205–210	20.8	20.8
HgCl ₂ ·2C ₄ H ₉ NO	...	45.0	45.8
HgBr ₂ ·2C ₄ H ₉ NO	Dec. 131–135	37.5	37.4

^a Inorganic halide dissolved in absolute alcohol.

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Investigations in the 1-Methylphenanthrene Series. I. The Conversion of Retene into 1-Methylphenanthrene

BY TORSTEN HASSELSTROM

A direct removal of the isopropyl group from the retene nucleus has been carried out successfully by refluxing retene with fuller's earth whereby 1-methylphenanthrene is obtained in satisfactory yields, together with propene. In this reaction a liquid hydrocarbon which was not investigated at this time is obtained as a by-product. The 1-methylphenanthrene was characterized through its picrate, quinone and phenazine prepared in the conventional manner. The melting points of the hydrocarbon and its derivatives agree, with exception of the phenazine, with those obtained by Pschorr¹ and Haworth² on the corresponding material obtained by complete synthesis.

The propene obtained in this reaction was absorbed in bromine and identified as propylene bromide.

Since retene is present in pine wood tar and can be obtained from abietic acid through dehydrogenation, 1-methylphenanthrene is easily produced from these natural products; it thus can

(1) Pschorr, *Ber.*, **39**, 3111 (1908).

(2) Haworth, *J. Chem. Soc.*, 1125 (1932).

be readily used as a source for synthetic work in the phenanthrene and related series.³

Acknowledgment.—Thanks are due to the Southern Pine Chemical Company, Jacksonville, Florida, for a supply of retene used in this investigation.

Experimental

1-Methylphenanthrene.⁴—Two hundred and fifty grams of retene and 50 g. of dehydrated fuller's earth were refluxed for nine hours. The gas developed was passed over bromine and in time was transformed into a colorless liquid. After cooling the semisolid brownish reaction product containing fuller's earth was dissolved in hexane and filtered. The filtrate was evaporated to remove most of the solvent and residues left standing in the ice box overnight after which the separated brownish colored crude hydrocarbon was removed by filtration; yield of crude material 97 g. This was recrystallized from hexane as fine glistening scales, m. p. 122–122.5° (cor.).

*Anal.*⁵ Calcd. for C₁₅H₁₂: C, 93.71; H, 6.29. Found: C, 93.55; H, 6.36.

The hexane solution from the above operation was evaporated and 118 g. of the residue was fractionated once in vacuum at 1 mm. pressure: I, 155–165°, 78 g. (solidified on standing); II, 165–175°, 20 g. (non-solidifying oil); III, 18 g. of residue. Only the first fraction was investigated at this time. It was recrystallized from hexane, m. p. 122–123° (cor.), and was found to be 1-methylphenanthrene since it did not depress the melting point of the analytical sample.

The 250 g. of retene yielded 62 g. of pure 1-methylphenanthrene.

The bromine absorption product was washed first with an aqueous sodium sulfite solution, then with a sodium carbonate solution and with water. The colorless liquid of propylene bromide was dried with anhydrous sodium sulfate and fractionated at ordinary pressure: b. p. 142–143° (uncor.); *d*₂₀ 1.9297; *n*_D²⁰ 1.52604.

Anal. Calcd. for: C₃H₅Br₂: Br, 79.16; Found: Br, 79.54.

Picrate of 1-Methylphenanthrene.—Brick red needles, recrystallized from alcohol, m. p. 139° (cor.).

Anal. Calcd. for: C₂₁H₁₆O₇N₃: N, 9.97. Found: N, 9.89.

The hydrocarbon recovered from the picrate melted at 122–122.5°.

1-Methylphenanthroquinone.—Dark reddish-brown needles, recrystallized from acetic acid, m. p. 192–193° decompn. (cor.).

Anal. Calcd. for: C₁₅H₁₀O₂: C, 81.06; H, 4.54. Found: C, 81.10; H, 4.54.

In cold concentrated sulfuric acid it dissolved to a dark green solution, which color disappeared upon dilution.

(3) Preliminary tests have shown, as expected, that 1-methylphenanthrene may be readily subjected to the Friedel-Crafts reactions, sulfonation, halogenation, etc.

(4) Subject matter for a U. S. Patent application.

(5) All analyses by Mr. S. Gottlieb, Columbia University, N. Y.

Phenazine.—Fluffy slightly yellowish needles recrystallized from glacial acetic acid, m. p. 183.5° (cor.).

Anal. Calcd. for: C₂₁H₁₄N₂: N, 9.52. Found: N, 9.97.

In cold concentrated sulfuric acid solution the color was burgundy red, which was lost on dilution.

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The Solubility of Carbon Dioxide in Aqueous Solutions of Sulfuric and Perchloric Acids at 25°

BY AARON E. MARKHAM AND KENNETH A. KOBE

The solubility of carbon dioxide and nitrous oxide in aqueous salt solutions was recently reported by Markham and Kobe.¹ They found that the gas solubility isotherms could be fitted by an equation of the form

$$\frac{S}{S_0} = am + \frac{1}{1 + bm} \quad (1)$$

in which *S* is the unit solubility, cc. gas (sc) dissolved by the amount of solution containing one gram of water, *m* is the salt molality, *a* and *b* are empirical constants derived from the data and specific for each curve. This equation fitted the isotherms within the limits of experimental error, about 0.2%, over the entire range of salt concentrations, up to 8 molal for sodium nitrate solutions.

It was the purpose of this work to determine the solubility of carbon dioxide in an aqueous solution of a strong electrolyte that is miscible in all proportions with water and whose gas solubility isotherm is not a continually decreasing function, as is the case with solutions of salts, and determine the range over which equation 1 can be fitted to the data.

Method and Results

Perchloric and sulfuric acids were Baker c. p. analyzed (A. C. S. specifications). The concentrated acid was standardized and diluted to give the desired solution, which was checked by a density determination.² The 100% sulfuric acid was made by adding fuming acid to the concentrated acid. The apparatus and technique were those described in the previous paper.¹ All measurements were made at a temperature of 25° and a partial gas pressure of 760 mm. The results are given in Table I. The Bunsen coefficient, *α*,

(1) Markham and Kobe, *THIS JOURNAL*, **63**, 449 (1941).

(2) For aqueous solutions of perchloric acid at 25°, see Markham, *ibid.*, **63**, 874 (1941).