ether gave positive Michler ketone tests. Tests with triphenylbismuth dichloride were negative.[2b]

Organolithium Compounds.—A solution of 8.2 g. (0.05 mole) of acetomesitylene in 25 cc. of ether was added dropwise to a refluxing ether solution of 0.061 mole of methyllithium. The evolved gas (methane by combustion) was 97% of the theoretical quantity. Hydrolysis of the clear ethereal solution yielded 85.5% of acetomesitylene. This experiment was checked.

From a related experiment using 8.0 g. (0.049 mole) of acetomesitylene and 0.10 mole of phenyllithium in 85 cc. of ether, there was recovered 7.8 g. or a 97% yield of acetomesitylene.

The lithium derivative prepared from 2.43 g. (0.015 mole) of acetomesitylene in 10 cc. of ether and 0.013 mole (15 cc. of 0.88 molar ether solution) of *n*-butyllithium or phenyllithium gave a weak but definite Michler ketone color test.

Phenylsodium.—To phenylsodium, prepared by stirring a mixture of 5.7 g. (0.25 g. atom) of sodium sand, 11.2 g. (0.10 mole) of chlorobenzene and 100 cc. of dry benzene for six hours at 35–40°, was added dropwise 24.3 g. (0.15 mole) of acetomesitylene in 25 cc. of benzene. The reaction was highly exothermic. After standing for twelve hours, samples gave good positive tests with Michler ketone. Hydrolysis, by the cautious addition of water, gave 20.9 g. or an 86% yield of acetomesitylene. No other identifiable products were isolated.

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The Antioxidant Properties of Antihemorrhagic Compounds

BY CALVIN GOLUMBIC

Many quinols possess the property of delaying the oxidative deterioration of fats and oils.[1,2,3] The antioxygenic capacity of the corresponding quinones is less than that of the quinols. However, the widespread occurrence of quinones in nature and the presence of vitamin K in alfalfa[4] and in soybean oil[5] prompted an investigation of the antioxygenic properties of these compounds,[6] particularly of those exhibiting vitamin K activity. The oxygen absorption method[7] was used to measure the induction period of the substrates with and without added stabilizers; lard, the ethyl esters of lard fatty acids, and purified fatty acids were used.

Effective antioxidants are found among the antihemorrhagic α-naphthols, α-naphthoquinones and *p*-benzoquinones and corresponding quinols (Table I). α-Naphthol and its homologs are by far the most active. The methyl α-naphthols are less effective than the parent compound and their action varies with the position of the methyl substituent. Similarly, the 2-methyl homolog of α-naphthohydroquinone exhibits diminished antioxygenic activity and the corresponding quinone, 2-methyl-1,4-naphthoquinone, is inactive. Similar relations between structure and antioxygenic activity have previously been observed in the benzene series.[2,3] Duroquinone and α-tocoquinone, reported to show slight vitamin K activity,[8,9] do not stabilize lard.[3]

TABLE I

THE ANTIOXYGENIC ACTION OF NAPHTHOLS, QUINONES AND QUINOLS ON LARD AND ON ETHYL ESTERS OF LARD FATTY ACIDS

Substrate	% Inhibitor added	Antioxygenic index at 75°[a]
Ethyl esters of lard fatty acids	0.02 α-naphthol	30
	.02 2-methyl-1-naphthol	24
	.02 3-methyl-1-naphthol	16
Lard	.10 α-naphthoquinone	1.5
	.04 α-naphthohydroquinone	7
	.10 2-methyl-1,4-naphthohydroquinone	1.5
Lard	.10 *p*-xyloquinone	1.5
	.04 *p*-xylohydroquinone	5
Lard	.02 β-naphthoquinone	8
	.10 β-lapachone	2.5
	.02 dehydro-iso-β-lapachone	2
	.02 pyrano-*o*-quinone (from α-tocopherol)	2

[a] The antioxygenic index is the ratio of the induction period in hours of the protected fat to that of the unprotected.

The effectiveness of benzenoid inhibitors is increased by the presence of additional hydroxyl groups[1]; this effect was not observed among the naphthenoid compounds. Thus, phthiocol and its corresponding quinol are not stabilizers. Other 2,3-disubstituted α-naphthoquinones, lomatiol, lapachol and the cyclic derivatives, α-lapachone and isopropylfuran α-naphthoquinone, are also inactive under the conditions used.

(1) H. A. Mattill, *J. Biol. Chem.*, **90**, 141 (1931).
(2) H. S. Olcott, THIS JOURNAL, **56**, 2492 (1934).
(3) C. Golumbic, *ibid.*, **63**, 1143 (1941).
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(5) H. J. Almquist and A. A. Klose, THIS JOURNAL, **61**, 1610 (1939).
(6) Grateful acknowledgment is extended to Dr. L. F. Fieser, Harvard University, for generous samples of lomatiol, lapachol and their cyclic derivatives. Samples of the methyl α-naphthols were kindly furnished by Dr. M. Tishler, Merck and Company, Rahway, N. J.
(7) R. B. French, H. S. Olcott and H. A. Mattill, *Ind. Eng. Chem.*, **27**, 724 (1935).
(8) R. Kuhn, K. Wallenfels, F. Weygand, Th. Moll and L. Hepding, *Naturwissenschaften*, **27**, 518 (1939).
(9) H. Dam, J. Glavind and P. Karrer, *Helv. Chim. Acta*, **23**, 224 (1940).

As was to be expected[1,2] compounds in the β-naphthoquinone series possess greater antioxygenic 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 antioxygenic action; in the benzene series the presence of a chroman ring markedly increases antioxygenic activity.

Obviously, no relation exists between antihemorrhagic and antioxygenic activity.

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Some Addition Compounds of Morpholine

BY HELMUT M. HAENDLER AND GEORGE MCP. SMITH

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 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
$ZnCl_2 \cdot 2C_4H_9NO$[a]	Softens 200–210, then melts	21.1	21.0
$ZnBr_2 \cdot 2C_4H_9NO$[a]	Dec. 230–240	16.4	16.3
$CdCl_2 \cdot 2C_4H_9NO$[a]	...	31.4	32.2
$CdBr_2 \cdot 2C_4H_9NO$	Dec. 250–252	25.2	24.8
$CdI_2 \cdot 2C_4H_9NO$	Dec. 205–210	20.8	20.8
$HgCl_2 \cdot 2C_4H_9NO$	...	45.0	45.8
$HgBr_2 \cdot 2C_4H_9NO$	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 Pschorr[1] and Haworth[2] 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

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