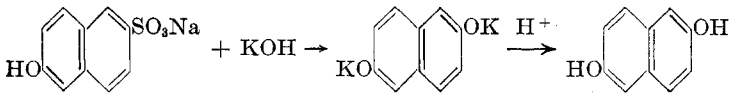
Dihydroxynaphthalenes and Some Derivatives as Gasoline Antioxidants

R. B. THOMPSON AND J. A. CHENICEK

Universal Oil Products Co., Riverside, Ill.

THE use of mono- and polyhydroxybenzenes as antioxidants for cracked hydrocarbon fuels is well known, and many data have been accumulated as to the type of structure necessary for high potency. However, use of dihydroxynaphthalenes and their derivatives has not been studied extensively. Because 1-naphthol is a much more potent inhibitor than phenol, an investigation was undertaken to determine whether the dihydroxynaphthalenes are more potent than the dihydroxybenzenes. The purpose of the present work was to prepare and test some dihydroxynaphthalenes and their derivatives in order to determine the structural features necessary for high potency.

Dihydroxynaphthalenes are described in the literature; ordinarily they may be prepared by alkali fusion of the corresponding sulfonic acids or naphtholsulfonic acids, as shown by 2,6-dihydroxynaphthalene (*5*) in Equation 1.



(1)

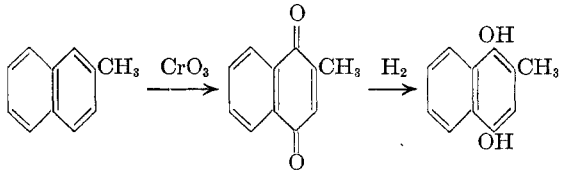
EXPERIMENTAL

The dihydroxynaphthalenes were prepared as described in the literature, except for the 1,7-compound (*6*). In this case the directions were modified as described by Fieser (*5*) for 2,6-dihydroxynaphthalene—the fused caustic was ladled directly into cold dilute hydrochloric acid.

Monoethers. The dihydroxynaphthalene dissolved in a dilute solution of sodium hydroxide was treated with slightly more than the equivalent quantity of methyl or ethyl sulfate.

Dihydroxydi- and Tetrahydronaphthalenes. The directions of Diels and Alder (*1*) were followed, except that methanol was substituted for benzene as the solvent. The ethers of these compounds were prepared in the same way as the monoethers.

2-Methyl-1,4-dihydroxynaphthalene was prepared by oxidation of 2-methylnaphthalene with chromic acid (*7*), followed by reduction of the quinone.



(2)

All induction periods were determined in the Universal Oil Products Co. oxygen bomb (*4*), using 0.025 weight % concentration of the antioxidant in a thermally cracked Pennsylvania gasoline having an uninhibited induction period of 100 minutes. Previous work in the Universal laboratories and that of Donahue (*2*) and others demonstrate that for a given gasoline the induction period correlates well with storage stability.

Dihydroxynaphthalenes with the hydroxy groups in all possible positions have been prepared. The 1,5- and 1,7-dihydroxynaphthalenes are not readily soluble in gasoline; but in spite of the fact that they do not stay dissolved in the gasoline, they greatly increase the induction period (Table I). The materials having the hydroxy groups on different rings are, in general, more effective in increasing the induction period than the ones with both hydroxy groups on the same ring.

1,5-Dihydroxynaphthalene would be a valuable gasoline antioxidant if its solubility could be improved. As the potency and solubility of phenols are ordinarily increased by alkylation, the 1,5-dihydroxynaphthalene was alkylated using *tert*-butyl alcohol and phosphoric acid as catalyst. This leads to a much more soluble product, which melts at 168–170° but is now relatively ineffective, 0.075% in the Pennsylvania cracked gasoline increasing the induction period by only 235 minutes. In addition, 1,6- and 1,8-dihydroxynaphthalenes were butylated. The butylated products are much more soluble but increase the induction period by only 220 and 80 minutes, respectively, in a concentration of 0.025%. Alkylation of 1-naphthol likewise greatly decreases its potency.

The effectiveness of hydroquinone in gasoline measured by the increase in induction period is greatly increased by alkylation of one of the hydroxy groups—that is, hydroquinone monomethyl ether is more potent and more soluble than hydroquinone (*3*, *8*). For comparison, monoalkyl ethers of all but one of the above dihydroxynaphthalenes were prepared and tested, with results shown in Table II.

The only compound showing an appreciably increased potency upon oxygen alkylation is the 1,4-dihydroxy compound; the

Table I. Dihydroxynaphthalenes as Gasoline Antioxidants

(Concentration 0.025%)

Compound	M. P., ° C.	Increase in Induction Period, Min.
1,2-Dihydroxynaphthalene	102–104	40
1,3-Dihydroxynaphthalene	122–123	5
2-Methyl-1,4-dihydroxynaphthalene	170	0
1,5-Dihydroxynaphthalene	258–260	1110
1,6-Dihydroxynaphthalene	132–133	305
1,7-Dihydroxynaphthalene	173–174	1315
1,8-Dihydroxynaphthalene	139–140	110
2,3-Dihydroxynaphthalene	157–158	10
2,6-Dihydroxynaphthalene	207–208	750
2,7-Dihydroxynaphthalene	184–185	45

Table II. Mono Ethers of Dihydroxynaphthalenes

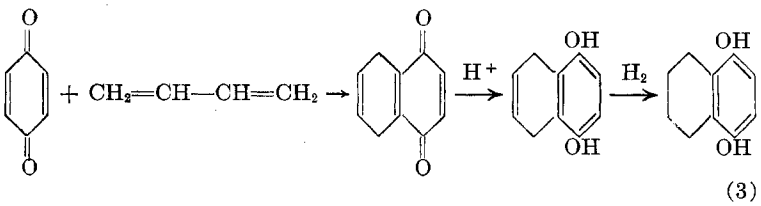
(Concentration 0.025%)

Compound	M.P., ° C.	B.P., ° C.	Mm.	Increase in Induction Period, Min.
1-Hydroxy-2-methyl-4-methoxynaphthalene	82– 83	130–135	2	190
1-Hydroxy-5-methoxynaphthalene	138–139	135–145	3	815
1-Hydroxy-5-ethoxynaphthalene	106–107	135–140	3	790
1-Hydroxy-7-methoxynaphthalene	...	120–130	2	905
1-Methoxy-7-hydroxynaphthalene				
2-Hydroxy-6-methoxynaphthalene	134–136	140–145	2	365
2-Hydroxy-1-methoxynaphthalene	...	105–110	3	90
1-Hydroxy-2-methoxynaphthalene				
1-Hydroxy-6-methoxynaphthalene	...	...	..	155
6-Hydroxy-1-methoxynaphthalene				
1-Hydroxy-8-methoxynaphthalene	57	...	..	20
2-Hydroxy-3-methoxynaphthalene	104–106	...	..	25
2-Hydroxy-7-methoxynaphthalene	121	...	..	10

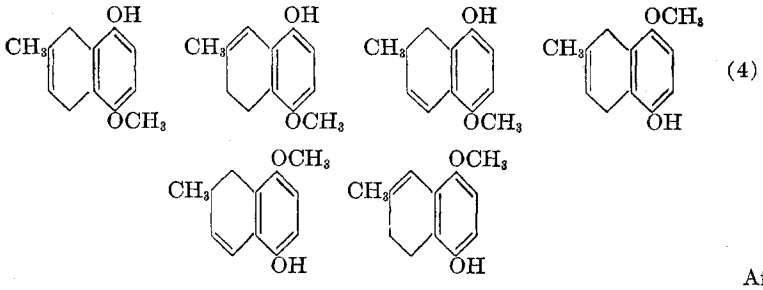
Table III. Dihydro- and Tetrahydro-1,4-dihydroxynaphthalenes as Gasoline Antioxidants

(Concentration 0.025%)

Compound	M.P., ° C.	Increase in Induction Period, Min.
1,4-Dihydroxy-5,8-dihydronaphthalene	204–206	0
1,4-Dihydroxy-5,6,7,8-tetrahydronaphthalene	170–171	0
1,4-Dihydroxy-6-methyl-5,8-dihydronaphthalene	173–174	0
1,4-Dihydroxy-6-methyl-5,6,7,8-tetrahydronaphthalene	172	0
1,4-Dihydroxy-5,7-dimethyl-5,8-dihydronaphthalene	113–115	0
1,4-Dihydroxy-5,7-dimethyl-5,6,7,8-tetrahydronaphthalene	134–135	0



(3)



(4)

potency of all others is decreased or only slightly changed, although the solubility of all is increased.

Alkylation of the monomethyl ether of 1,5-dihydroxynaphthalene using tert-butyl alcohol yields a product melting at 74–75°, which in 0.075% concentration increased the induction period of the Pennsylvania gasoline by only 250 minutes. Butylation of 1-hydroxy-8-methoxynaphthalene gave a viscous liquid product of about the same potency as the starting ether.

Partially hydrogenated derivatives of 1,4-dihydroxynaphthalene are readily available through the reaction of *p*-benzoquinone with 1,3-dienes, as Equation 3 shows (*1*).

In general, all these reactions go readily in excellent yield. The dihydro and tetrahydro compounds have been prepared from three different dienes to give the compounds of Table III.

Like 2-methyl-1,4-dihydroxynaphthalene and hydroquinone, these materials show no potency in gasoline by the induction period method. When one of the hydroxy groups is alkylated, they become effective inhibitors. This alkylation, in which an alkaline solution is used, in most cases produces a mixture of isomers differing in position of the double bond, position of the methoxy, or a combination of both. For example, from 1,4-dihydroxy-6-methyl-5,8-dihydronaphthalene the following isomers may be expected upon alkylation in alkaline solution.

The fact that the double bond is shifted into the conjugated position was shown by the ultraviolet absorption spectrum. The existence of this mixture of isomers offers a ready explanation for the wide melting range of the products of Table IV which can form isomers. Conversely, if no isomers are possible, the product melts in a relatively close range.

The monoalkyl ethers of the dihydroxydihydronaphthalenes all have rather good potencies and are readily soluble in gasoline and not readily soluble in dilute sodium hydroxide. Two points deserve mention: The ethoxy compounds are with only one exception slightly more effective than the methoxy compounds, and alkylation of one hydroxy is much more effective in producing a good inhibitor than in the case of 2-methyl-1,4-dihydroxy-naphthalene.

In continuing the alkylation of these materials 1-methoxy-4-hydroxy-6-methyl-5,6,7,8-tetrahydronaphthalene was treated with *tert*-butyl alcohol and phosphoric acid to achieve carbon alkylation. This reaction gave two products, one soluble and the other insoluble in Claisen solution. However, both materials are less potent inhibitors than the starting product, increasing the induction period by only 475 minutes.

CONCLUSIONS

After synthesis and testing of a considerable number of dihydroxynaphthalenes, the following conclusions can be drawn.

The introduction of an alkyl group onto any nuclear carbon atom decreases the potency of the compound.

For the 1,4-dihydroxynaphthalene, the unsubstituted compound is ineffective, alkylation of one hydroxy group imparts a slight potency, and with one hydroxy alkylated the partially hydrogenated compounds are much more effective.

For dihydroxynaphthalenes having the hydroxy groups on different rings, the unsubstituted compounds show some inhibiting potency, and alkylation of one of the hydroxy groups decreases the potency.

Table IV. Ethers of Dihydro- and Tetrahydro-1,4-dihydroxynaphthalene

(Concentration 0.025%)

Compound[a]	M.P., ° C.	B.P., ° C.	Mm.	Increase in Induction Period, Min.
1-Methoxy-4-hydroxydihydronaphthalene[b]	125–130	...	..	780
1-Ethoxy-4-hydroxydihydronaphthalene	124–132	...	..	850
1-Methoxy-4-hydroxy-5,6,7,8-tetrahydronaphthalene	112–113	...	..	785
1-Ethoxy-4-hydroxy-5,6,7,8-tetrahydronaphthalene	108–110	...	..	790
1-Methoxy-4-hydroxy-6-methyldihydronaphthalene	85– 95	125–130	2	690
1-Ethoxy-4-hydroxy-6-methyldihydronaphthalene	88– 94	125–128	2	765
1-Methoxy-4-hydroxy-6-methyl-5,6,7,8-tetrahydronaphthalene	80– 90	125–130	2	690
1-Ethoxy-4-hydroxy-6-methyl-5,6,7,8-tetrahydronaphthalene	95–100	...	..	710
1-Methoxy-4-hydroxy-5,7-dimethyldihydronaphthalene	...	125–130	2	705
1-Ethoxy-4-hydroxy-5,7-dimethyldihydronaphthalene	...	125–130	2	710
1-Methoxy-4-hydroxy-5,7-dimethyl-5,6,7,8-tetrahydronaphthalene	...	113–117	2	755
1-Ethoxy-4-hydroxy-5,7-dimethyl-5,6,7,8-tetrahydronaphthalene	...	122–126	2	700

[a] In the dihydronaphthalenes, the double bond may be in any of the three possible positions and the substances are mixture of isomers.

[b] By starting with toloquinone, 1-methoxy-2- and 3-methyl-4-hydroxydihydronaphthalenes were prepared. These compounds are almost identical with 1-methoxy-4-hydroxydihydronaphthalene in antioxidant potency.

LITERATURE CITED

(1) Diels, O., and Alder, K., *Ber.*, **62**, 2361 (1929).
(2) Donahue, R. W., "Correlation of Induction Tests with Motor Fuel Stability," Symposium on Gum and Storage Stability Characteristics of Motor Gasoline, Technical Committee A, ASTM Committee D2, Philadelphia, Pa., Feb. 15, 1954.
(3) Dryer, C. G., Morrell, J. C., Egloff, G., and Lowry, C. D., Jr., IND. ENG. CHEM., **27**, 15, 315 (1935).
(4) Egloff, G., Morrell, J. C., Lowry, C. D., Jr., and Dryer, C. G., *Ibid.*, **24**, 1375 (1932).
(5) Fieser, L. F., *J. Am. Chem. Soc.*, **50**, 461 (1928).
(6) Morgan, G. T., and Vining, D. C., *J. Chem. Soc.*, **119**, 1709 (1921).
(7) Nikolaev, N. S., *J. Gen. Chem. (U.S.S.R.)*, **15**, 654(1945).
(8) Rosenwald, R. H., and Chenicek, J. A. (to Universal Oil Products Co.). U. S. Patent **2,310,710** (Feb. 9, 1943).

RECEIVED for review July 31, 1954.
ACCEPTED February 10, 1955.