$$na^2\delta + (n-1)a\delta(1 - S_F/s_D) + (n-2)\delta(1 - S_F/s_D) =$$

$$\frac{n(n+1)}{2}a^2\delta_1 + \frac{(n-1)(n+2)}{2}a\delta_1(1 - S_F/s_D) +$$

$$\frac{(n-2)(n+3)}{2}\delta_1(1 - S_F/s_D)$$

Therefore

$$\frac{\bar{\delta}}{\delta} = \frac{n(n+1)a^2 + (n-1)(n+2)a(1 - S_F/s_D) + (n-2)(n+3)(1 - S_F/s_D)}{2(na^2 + (n-1)a(1 - S_F/s_D) + (n-2)(1 - S_F/s_D)}$$

$$= \frac{n^2[a^2 + (1 - S_F/s_D)(a+1)] + n[a^2 + (1 - S_F/s_D)(a+1)] - (1 - S_F/s_D)(2a+6)}{2\{n[a^2 + (1 - S_F/s_D)(a+1)] - (1 - S_F/s_D)(a-2)\}}$$

$$= \frac{n+1}{2}\Big[\text{neglecting terms } (1 - S_F/s_D)(2a+6) \text{ and } (1 - S_F/s_D)(a-2)\Big]$$

If $n = 4$, $a = 1.5$, and $S_F/s_D = 0.05$ find a_{mean}.

Exact formula gives $a_{mean} = 2.494$, approximately 2.500 (error is 0.23%).

$$\bar{\delta} = \frac{n\delta_1 + \delta_1}{2} \text{ or } a_0 + \bar{\delta} = \frac{(a_0 + n\delta_1) + (a_0 + \delta_1)}{2} = \frac{a_n + a_1}{2}$$

Alkyl Phenols as Antioxidants

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A number of alkyl phenols with methyl and butyl substituents in the 2-, 4-, and 6-positions were examined as to effectiveness in the stabilization of cracked gasoline. The following factors were considered regarding the effect of structure on potency—number of substituents, size, position, and configuration of substituents. Those structural factors were considered which impart maximum potency to the alkyl phenol.

CERTAIN alkyl phenols possess some desirable properties as gasoline antioxidants, especially with regard to such properties as high stability toward darkening when exposed to air in either dilute or concentrated form, high solubility in gasoline, and inertness toward acidic and alkaline reagents. On the other hand, alkyl phenols are not outstanding in their potency as measured in the accelerated oxygen bomb test. Consequently, in any attempt to use alkyl phenols on a commercial basis for inhibiting motor fuel, it is essential to select a phenol of such structure that maximum potency is realized, for the alkyl phenol is under handicap in competing with the more potent antioxidants used at present. This investigation is an attempt to determine what structural factors, if any, are involved in effecting maximum potency of the alkyl phenol. In this discussion, the relationship between potency and structure will be considered for those phenols which are substituted in the 2-, 4-, and 6-positions, with methyl and butyl groups as the substituent alkyl groups.

The synthesis and properties of the alkyl phenols are summarized in Table I. The designations A, B, and C indicate general procedure used in preparation. Procedure A is an alkylation with isobutylene and *n*-butylene, or the corresponding alcohols, to give *tert*-butyl and *sec*-butyl derivatives, respectively. Procedure B is the preparation of a butyryl phenol followed by Clemmensen reduction. Procedure C is the preparation via formation of a methylallyl ether followed by rearrangement and reduction. The boiling points and melting points reported are uncorrected. The phenyl urethanes were the derivatives more easily prepared since the aryloxyacetic acids of the highly alkylated phenols were difficult to obtain.

The alkyl phenols thus prepared were tested as to potency in the accelerated oxygen bomb (U.O.P. Method H-6-40) (*24*) using a Pennsylvania thermally cracked gasoline. This gasoline, contacted with a methyl alcohol–water solution of potassium hydroxide to remove all natural inhibitors, possessed an induction period of 55 minutes; due precautions were taken to avoid changes in the base stock during testing. Potencies were determined in at least six concentrations, generally eight or twelve concentrations, ranging from 10 to 1000 parts of inhibitor per million parts of gasoline, except for antioxidants of low potencies, in which case concentrations up to 2000 were used.

By use of the logarithmic equation

$$\log y = r + s \log x$$

in which y is the length of the induction period in minutes and x is the inhibitor concentration in parts of inhibitor per million parts of gasoline, the concentrations of alkyl phenols required to give a 300-minute induction period have been determined. The relative potency was determined by comparing concentrations relative to that of 2,4-dimethyl-6-*tert*-butylphenol, which required 71 p.p.m. to obtain a 300-minute induction period. The precision of these potency values as determined in this motor fuel is estimated to be 10% except for those alkyl phenols of low potency. The relative potencies, as listed in Table II, do vary greatly from values of less than 0.05 to that of the standard. It is evident that structure of the phenol does greatly affect its antioxidant activity.

In considering the effect of structure on potency there are four factors which will be considered: number of substituents

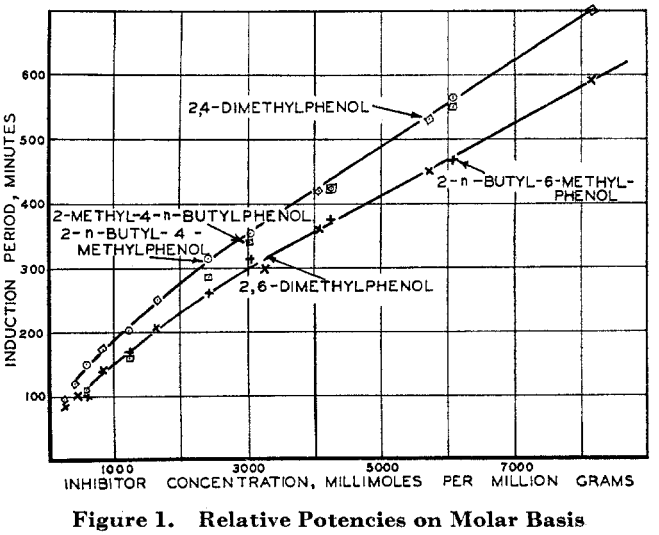

Figure 1. Relative Potencies on Molar Basis

TABLE I. PREPARATION AND PROPERTIES OF ALKYL PHENOLS

Compound	Physical Properties: Melting point, °C., Found	Physical Properties: Boiling point, °C.	n_D^{20}	Method of Preparation[a]	Yield[a], %	Literature Reference	Derivative, Melting Point, ° C.: Aryloxyacetic acid	Derivative, Melting Point, ° C.: Phenylurethan
2,4-Dimethylphenol	.....	.....	1.5407	..	.....	(7)	139.5-141	.....
2,6-Dimethylphenol	44-45.5	.....	....	..	.....	(7)	137.5-139	.....
Mesitol	71-72	.....	....	..	.....	(7, 20)	148.5-149	140-141
2-*n*-Butylphenol	.....	227-230	1.5219	B	64	(14, 17)	105-106	.....
2-Isobutylphenol	.....	117/23	1.5176	C	E-62 R-73.5	(2)	95-96	.....
2-*sec*-Butylphenol	.....	.....	....	..	.....	(13, 19)	111	.....
2-*tert*-Butylphenol	.....	62/2	1.5238	A	Low	(13)	144-145	.....
4-*n*-Butylphenol	.....	238-241	1.5187	B	70	(10, 15)	80-81	113-113.5
4-Isobutylphenol	51-52	235-239	....	B	70	(1, 10)	106-107	141-142
4-*sec*-Butylphenol	59-59.5	.....	....	..	.....	(7, 14)	61.5-62.5	103-104
4-*tert*-Butylphenol	.....	.....	....	..	.....	(7)	85-86.5	.....
2-Methyl-6-*n*-butylphenol	.....	82-84/3.5	1.5169	B	.....	(4)	.....	111-112
2-Methyl-6-isobutylphenol	41.5-42	.....	....	C	E70.5 R70	(2)	.....	101.5-102.5
2-Methyl-6-*sec*-butylphenol	.....	81.5-82/2.5 229-231	1.5197	A	10 (Estd.)	.....	.....	109 - 110
2-Methyl-4-*n*-butylphenol	.....	89-91/3	1.5194	B	45	(4)	.....	127
2-Methyl-4-isobutylphenol	.....	93-95/3	1.5170	B	54.5	(18)	.....	141-142
2-Methyl-4-*sec*-butylphenol	.....	93/2.5 239	1.5217	A	20 (Estd.)	(18)	95-96	120.5-121
2-Methyl-4-*tert*-butylphenol	27-28.5	235-237	....	A	34	(3, 9, 11, 23)	103-104	139.5-140.5
2-*n*-Butyl-4-methylphenol	16	140-141/19	1.5205	B	55	(4)	.....	83-84
2-Isobutyl-4-methylphenol	41-41.5	120/17.5	....	C	E59 R83.5	(2)	111	114-115
				B	54			
2-*sec*-Butyl-4-methylphenol	43-44	234	....	A	44	(19)	81-82	93-94
2-*tert*-Butyl-4-methylphenol	51-52	.....	.....	A	66	(11, 23)	128-130	153-154
2,4-Dimethyl-6-*n*-butylphenol	.....	83/2	1.5175	B	K62 D50	(22)	.....	98-99
2,4-Dimethyl-6-isobutylphenol	67-67.5	.....	....	B	K79 D80	(2)	.....	102-103
2,4-Dimethyl-6-*sec*-butylphenol	.....	91-92.5/2.5	1.5189	C	E62.5 R72	.....	.....	112-113
2,4-Dimethyl-6-*tert*-butylphenol	.....	.....	1.5204	..	.....	(11, 23)	.....	170-170.5
2,6-Dimethyl-4-*tert*-butylphenol	81-82	.....	....	A	41	(6, 11)	.....	154-155
2-*tert*-Butyl-4-*n*-butylphenol	.....	270-272	1.5089	A	39	.....	.....	136-137
2-*tert*-Butyl-4-isobutylphenol	.....	259-260 105-106/2.5	1.5070	A	36	.....	.....	155-155.5
2-*tert*-Butyl-4-*sec*-butylphenol	.....	255-256	1.5078	A	31.5	.....	.....	126-127
2,4-Di-*tert*-butylphenol	56	.....	....	..	.....	(11)	175-175.5	141-142
2,4-Di-*tert*-butyl-6-methylphenol	52	.....	....	A	.....	(11, 21)	.....	.....
2,6-Di-*tert*-butyl-4-methylphenol	69-70	.....	....	A	.....	(11, 21)	.....	.....
2,4,6-Tri-*tert*-butylphenol	128-129	.....	....	A	.....	(11, 21)	.....	.....

[a] A, alkylation of phenol with butylene or butyl alcohol; B, reduction of butyrylphenol; C, rearrangement of methylalkyl ether and reduction; E, yield of methylallyl ether; R, yield on rearrangement; K, yield of butyrylphenol; D, yield on Clemmensen reduction.

(up to three); size of substituents (methyl or butyl); position of substituents (2-, 4-, or 6-position); and configuration of substituents (in butyl groups).

The comments on these four points are obtained by inspection of the relative potencies as found in Table II where the comparison of potencies is made on a weight basis with no correction for differences in molecular weights. For comparison on an equivalent basis, one may refer to Relative Molar Potencies in Table III, the calculations of which are explained later.

NUMBER OF SUBSTITUENTS. The potency of a phenol is increased by insertion of alkyl groups. Furthermore, this effect, as stated in the work of others (*5*, *8*) is more than additive—i.e., the stabilization as afforded by 2,4-dimethylphenol is greater than the summation of that afforded by *o*-cresol and *p*-cresol. Likewise, the addition of a third methyl group increases the potency to a greater extent than expected by addition of the potencies of xylenol and cresol.

This effect can also be found in the butylated phenols. For example, the effectiveness of a 2-*tert*-butyl-4-methylphenol is greater than predicted by the combined potencies of 2-*tert*-butylphenol and *p*-cresol. As shown later, there is a limit to which this effect can be applied.

The potency of a phenol is increased by increasing the number of substituents and the increase is greater than that calculated as a simple additive effect.

SIZE OF SUBSTITUENT. In order to determine the effect of the size of the group, a comparison can be made between the corresponding methyl- and *n*-butylphenols. The normal butyl group can be considered an extended or lengthened methyl group. In order to make a valid comparison, a factor to correct for the increase in molecular weight should be used. Such correction is taken into account in Figure 1 where induction period is plotted against concentration in millimoles of inhibitor per million grams of gasoline. On this basis, of the 2,4-dialkyl phenols considered in Figure 1, all possess similar potencies and the same condition holds for the two 2,6-dialkyl phenols. Like-

TABLE II. RELATIVE POTENCIES OF ALKYL PHENOLS

Phenol	Relative Potency
Phenol	<0.01
2-Methylphenol	0.08
4-Methylphenol	0.06
2,4-Dimethylphenol	0.28
2,6-Dimethylphenol	0.21
Mesitol	0.72
2-*n*-Butylphenol	0.06
2-Isobutylphenol	0.06
2-sec-Butylphenol	0.08
2-*tert*-Butylphenol	0.14
4-*n*-Butylphenol	0.04
4-Isobutylphenol	0.03
4-*sec*-Butylphenol	0.03
4-*tert*-Butylphenol	0.04
2-Methyl-6-*n*-butylphenol	0.14
2-Methyl-6-isobutylphenol	0.15
2-Methyl-6-*sec*-butylphenol	0.17
2-Methyl-4-*n*-butylphenol	0.17
2-Methyl-4-isobutylphenol	0.12
2-Methyl-4-*sec*-butylphenol	0.08
2-Methyl-4-*tert*-butylphenol	0.13
2-*n*-Butyl-4-methylphenol	0.19
2-Isobutyl-4-methylphenol	0.19
2-*sec*-Butyl-4-methylphenol	0.26
2-*tert*-Butyl-4-methylphenol	0.42
2,4-Dimethyl-6-*n*-butylphenol	0.46
2,4-Dimethyl-6-isobutylphenol	0.55
2,4-Dimethyl-6-*sec*-butylphenol	0.49
2,4-Dimethyl-6-*tert*-butylphenol	1.00
2,6-Dimethyl-4-*tert*-butylphenol	0.12
2-*tert*-Butyl-4-*n*-butylphenol	0.40
2-*tert*-Butyl-4-isobutylphenol	0.27
2-*tert*-Butyl-4-*sec*-butylphenol	0.27
2,4-Di-*tert*-butylphenol	0.30
2,4-Di-*tert*-butyl-6-methylphenol	0.28
2,6-Di-*tert*-butyl-4-methylphenol	0.59
2,4,6-Tri-*tert*-butylphenol	0.28

TABLE III. RELATIVE MOLAR POTENCIES OF ALKYL PHENOLS

Substituent	Relative Molar Potency in Range c = 100 to 1000[a]
None	3.5 − 1.0 log c
2-methyl	−2.0 + 2.5 log c
4-methyl	5.0 − 0.5 log c
2,4-dimethyl	26.5 − 3.0 log c
2,6-dimethyl	17.0 − 1.0 log c
2,4,6-trimethyl	71.0 − 7.0 log c
2-*n*-butyl	10.5 − 2.0 log c
2-isobutyl	3.0 + 1.0 log c
2-*sec*-butyl	2.5 + 1.5 log c
2-*tert*-butyl	−0.5 + 5.5 log c
4-*n*-butyl	2.0 + 0.5 log c
4-isobutyl	0.0 + 1.0 log c
4-*sec*-butyl	2.0 + 0.0 log c
4-*tert*-butyl	3.5 + 0.0 log c
2-methyl-6-*n*-butyl	13.5 + 0.0 log c
2-methyl-6-isobutyl	30.5 − 6.0 log c
2-methyl-6-*sec*-butyl	14.5 + 0.5 log c
2-methyl-4-*n*-butyl	11.0 + 2.0 log c
2-methyl-4-isobutyl	12.0 + 0.0 log c
2-methyl-4-*sec*-butyl	10.5 − 1.0 log c
2-methyl-4-*tert*-butyl	18.5 − 2.0 log c
2-*n*-butyl-4-methyl	24.5 − 2.5 log c
2-isobutyl-4-methyl	19.5 − 0.5 log c
2-*sec*-butyl-4-methyl	37.5 − 5.0 log c
2-*tert*-butyl-4-methyl	20.5 + 8.5 log c
2,4-dimethyl-6-*n*-butyl	39.0 + 3.5 log c
2,4-dimethyl-6-isobutyl	71.0 − 7.0 log c
2,4-dimethyl-6-*sec*-butyl	63.0 − 6.0 log c
2,4-dimethyl-6-*tert*-butyl	100.0 + 0.0 log c
2,6-dimethyl-4-*tert*-butyl	33.5 − 7.5 log c
2-*tert*-butyl-4-*n*-butyl	33.0 + 4.5 log c
2-*tert*-butyl-4-isobutyl	13.5 + 8.0 log c
2-*tert*-butyl-4-*sec*-butyl	6.5 + 9.5 log c
2,4-di-*tert*-butyl	21.0 + 6.0 log c
2,4-di-*tert*-butyl-6-methyl	73.5 − 15.5 log c
2,6-di-*tert*-butyl-4-methyl	74.0 + 1.0 log c
2,4,6-tri-*tert*-butyl	27.5 + 6.0 log c

[a] c is concentration of phenol under consideration.

wise, a comparison can be made of 2-*tert*-butyl-4-methylphenol and 2-*tert*-butyl-4-*n*-butylphenol on a molar basis and the two compounds are of equal potency.

It thus appears that an increase in length of a substituent from a methyl group to a normal butyl group is of minor consequence with due correction for molecular weights.

POSITION OF SUBSTITUENT. Examination of the relative potencies reveals that substitution in the ortho position for the first substituent is more effective in raising potency than substitution in the para position. The ortho alkyl phenols are more potent than the para alkyl phenols.

In substitution of the second group, there is a small difference whether the group is placed in the ortho or para positions. In the xylenols, the 2,4-isomer is more potent than the 2,6-isomer, a condition shown in Figure 1. In the *n*-butyl-*o*-cresols, differences between the 2,6- and 2,4-isomers are evident, with the 2,4-isomer the more potent. However, the position of the substituent is not of major importance, for the superiority of the 2,4-isomer is noticeable but not outstanding.

CONFIGURATIONS OF SUBSTITUENTS. The following observations can be made as to the effect of branching of the butyl group:

An increase in branching of the ortho substituent in the monoalkyl phenols increases the potencies. The potency of the secondary isomer is slightly more than the normal and iso isomers, and that of the tertiary isomer is outstanding. In the case of para monoalkyl compounds, the potencies are all very similar. The effect of the *tert*-butyl configuration is lacking in this position.

In the case of the methylbutylphenols, there is no pronounced effect of configuration of the three 2,6-isomers (the *tert*-butyl isomer is missing) and the four 2-methyl-4-butyl isomers. Of the 2-butyl-4-methylphenols, the tertiary configuration prompts high potency, followed by the secondary configuration.

In the case of the four 2-*tert*-butyl-4-butylphenols, the effect of configuration is noticeable but not critical. The *n*-butyl isomer is the most potent, followed by the *tert*-butyl isomer.

In the case of the 2,4-dimethyl-6-butylphenols, maximum potency is obtained with the tertiary configuration with identical potencies for the other three configurations.

The effect of the *tert*-butyl group and its position is pronounced in some of the trisubstituted phenols. The potency of 2,4-di-*tert*-butyl-6-methylphenol is about one half that of its position isomer, 2,6-di-*tert*-butyl-4-methylphenol. The potency of 2,6-dimethyl-4-*tert*-butylphenol is about one eighth that of its isomer, 2,4-dimethyl-6-*tert*-butylphenol. For the trisubstituted phenols it appears that the presence of a *tert*-butyl group in the 4-position has a detrimental effect.

In regard to configuration, there are indications that: the increase in inhibitor potency by insertion of an alkyl group in a position ortho to the hydroxyl group is at the maximum with a tertiary butyl group; the differences between the ortho normal, iso, and secondary butyl derivatives are small, with the latter often more potent; in general, there is but small effect of structure variation of the alkyl group in the 4-position.

It was of interest to evaluate the constants in each of the following two equations, which have been shown to apply in correlating length of induction period and inhibitor concentration (*16*).

$$\log y = r + s \log x$$

$$y = a + bx + c \log x$$

An attempt was made to consider values of the constants in relation to structure and potency. However no definite structural effect is reflected with consistency in the values of the constants. General structural effects have been observed but they have not been of value in consideration of individual compounds. A typical general trend is the effect of the number of substituents on the average values of the constants as follows:

	r	s	a	b	c
Monoalkyl phenols	0.480	0.645	+ 30	0.234	7.2
Dialkyl phenols	0.873	0.632	− 86	0.430	94.3
Trialky phenols	1.163	0.596	−132	0.599	161.8

It is possible to express the effect of structure on potency by a compilation based on the principle that the various structural units exert a calculable influence on potency—i.e., the inhibitor potency can be expressed as the resultant of the influence of the individual substituents in the benzene ring.

The relative molar potency for each compound was calculated, with 2,4-dimethyl-6-*tert*-butylphenol as standard, by use of the equation

$$\text{Relative molar potency} = \frac{\text{p.p.m. of 2,4-dimethyl-6-}tert\text{-butylphenol}}{\text{p.p.m. of other phenol}} \times M \times 100$$

where the inhibitor concentrations are those required to obtain a certain induction period and M is a factor to bring all compounds on an equimolar basis and is calculated by dividing the molecular weight of the phenol in question by the molecular weight of the 2,4-dimethyl-6-*tert*-butylphenol.

The relative molar potency varied linearly with log of the con-

TABLE IV. EFFECTS OF SUBSTITUENTS

Substituent Group	Position	Effect	Value of Effect[a]
Hydrogen	2	*A*	0.0 + 0.0 log c
	4	*B*	2.0 − 0.5 log c
	6	*C*	0.0 + 0.0 log c
Methyl	2	*A*	3.0 + 0.5 log c
	4	*B*	10.5 − 2.0 log c
	6	*C*	5.5 − 1.0 log c
n-Butyl	2	*A*	2.5 + 0.5 log c
	4	*B*	2.5 + 0.5 log c
	6	*C*	−1.5 + 1.5 log c
Isobutyl	2	*A*	0.0 + 1.5 log c
	4	*B*	2.0 + 0.0 log c
	6	*C*	5.0 − 0.5 log c
sec-Butyl	2	*A*	3.0 + 0.5 log c
	4	*B*	−4.0 + 2.0 log c
	6	*C*	2.5 + 0.0 log c
tert-Butyl	2	*A*	10.0 + 2.5 log c
	4	*B*	6.5 − 1.5 log c
	6	*C*	−4.5 + 1.0 log c

[a] c is concentration of phenol under consideration.

TABLE V. CALCULATED RELATIVE MOLAR POTENCIES OF PHENOLS

Substituent	c^a = 100 From curve	Calcd.	Diff.	c = 316.2 From curve	Calcd.	Diff.	c = 1000 From curve	Calcd.	Diff.
None	1.5	0.5	−1.0	1.0	0.5	− 0.5	0.5	0.5	0.0
2-methyl	3.0	5.0	+2.0	4.0	5.0	+ 1.0	5.5	5.0	− 0.5
4-methyl	4.0	6.5	+2.5	3.0	5.5	+ 2.5	3.5	4.5	+ 1.0
2,4-dimethyl	20.5	21.0	+0.5	19.5	19.5	0.0	17.5	18.0	+ 0.5
2,6-dimethyl	15.0	17.0	+2.0	14.5	16.0	+ 1.5	14.0	15.0	+ 1.0
2,4,6-trimethyl	57.0	56.0	−1.0	53.5	51.0	− 2.5	50.0	46.0	− 4.0
2-*n*-butyl	6.5	4.5	−2.0	5.5	4.5	− 1.0	4.5	4.5	0.0
2-isobutyl	5.0	4.0	−1.0	5.0	4.5	− 0.5	6.0	5.0	− 1.0
2-*sec*-butyl	5.5	5.0	−0.5	6.5	5.0	− 1.5	7.0	5.0	− 2.0
2-*tert*-butyl	10.5	16.0	+5.5	13.0	17.5	+ 4.5	16.0	18.0	+ 2.0
4-*n*-butyl	3.0	3.5	+0.5	3.0	3.5	+ 0.5	3.5	4.0	+ 0.5
4-isobutyl	2.0	2.0	0.0	2.5	2.0	− 0.5	3.0	2.0	− 1.0
4-*sec*-butyl	2.0	0.0	−2.0	2.0	1.0	− 1.0	2.0	2.0	0.0
4-*tert*-butyl	3.5	3.5	0.0	3.5	3.0	− 0.5	3.5	2.0	− 1.5
2-methyl-6-*n*-butyl	13.5	13.0	−0.5	13.5	14.5	+ 1.0	13.5	16.0	+ 2.5
2-methyl-6-isobutyl	18.5	18.0	−0.5	15.5	17.5	+ 2.0	12.5	17.0	+ 4.5
2-methyl-6-*sec*-butyl	15.5	15.0	−0.5	16.0	15.0	− 1.0	16.0	15.0	− 1.0
2-methyl-4-*n*-butyl	15.0	15.0	0.0	16.0	16.0	0.0	17.0	17.0	0.0
2-methyl-4-isobutyl	12.0	12.0	0.0	12.0	12.5	+ 0.5	12.0	13.0	+ 1.0
2-methyl-4-*sec*-butyl	8.5	8.0	−0.5	8.0	10.5	+ 2.5	7.5	13.0	+ 5.5
2-methyl-4-*tert*-butyl	14.5	15.0	+0.5	13.5	14.0	+ 0.5	12.5	13.0	+ 0.5
2-*n*-butyl-4-methyl	19.5	20.0	+0.5	18.0	18.5	+ 0.5	17.0	17.0	0.0
2-isobutyl-4-methyl	18.5	19.0	+0.5	18.0	18.5	+ 0.5	18.0	18.0	0.0
2-*sec*-butyl-4-methyl	27.5	21.0	−6.5	25.0	19.5	− 5.5	22.5	18.0	− 4.5
2-*tert*-butyl-4-methyl	37.5	43.0	+5.5	41.5	43.5	+ 2.0	46.0	44.0	− 2.0
2,4-dimethyl-6-*n*-butyl	46.0	48.0	+2.0	47.5	48.0	+ 0.5	49.5	48.0	− 1.5
2,4-dimethyl-6-isobutyl	57.0	58.0	+1.0	54.0	54.0	0.0	50.0	50.0	0.0
2,4-dimethyl-6-*sec*-butyl	51.0	52.0	+1.0	48.0	49.0	+ 1.0	45.0	46.0	+ 1.0
2,4-dimethyl-6-*tert*-butyl	100.0	100.0	0.0	100.0	98.0	− 2.0	100.0	96.0	− 4.0
2,6-dimethyl-4-*tert*-butyl	18.5	22.0	+3.5	14.5	20.0	+ 5.5	11.0	18.0	+ 7.0
2-*tert*-butyl-4-*n*-butyl	42.0	37.0	−5.0	44.0	40.0	− 4.0	46.5	43.0	− 3.5
2-*tert*-butyl-4-isobutyl	29.5	34.0	+4.5	33.5	36.5	+ 3.0	37.5	39.0	+ 1.5
2-*tert*-butyl-4-*sec*-butyl	27.5	30.0	+2.5	32.5	34.5	+ 2.0	38.0	39.0	+ 1.0
2,4-di-*tert*-butyl	33.0	37.0	+4.0	36.0	38.0	+ 2.0	39.0	39.0	0.0
2,4-di-*tert*-butyl-6-methyl	42.5	44.0	+1.5	34.0	44.0	+10.0	27.0	44.0	+17.0
2,6-di-*tert*-butyl-4-methyl	76.0	76.0	0.0	76.5	79.0	+ 2.5	77.0	82.0	+ 5.0
2,4,6-tri-*tert*-butyl	39.5	32.0	−7.5	42.5	34.0	− 8.5	45.5	36.0	− 9.5
		Average	±1.85		Average	±2.03		Average	±2.47

[a] c = p.p.m. of inhibitor—i.e., concentration of phenol under consideration.

centration of the phenol under consideration in the range of 100 to 1000 p.p.m. By examination of such data, one can express the relative molar potency of each compound as shown in Table III. Certain compounds increase in relative effectiveness with increase in concentration whereas others show a decrease.

These relative molar potencies, which are determined experimentally, can be calculated with a reasonable degree of success by purely mathematical means. The following equation can be used to calculate the relative molar potencies of phenols substituted by methyl and butyl groups in the 2-, 4-, and 6-positions.

$$\text{Relative molar potency} = (A + B + C)2^{2-H-R+HR}$$

where A, B, and C are the effects of individual substituents in the 2-, 4-, and 6-positions, H is the number (either 0, 1, 2, or 3) of hydrogen atoms in the 2-, 4-, and 6-positions, and R is the number (either 0 or 1) of butyl groups in the 4-position. The values of A, B, and C, which represent the effect of the individual substituents in the 2-, 4-, and 6-positions, were selected empirically to give minimum deviation upon substitution in the equation. The values for these effects are given in Table IV.

In making the calculations, the 2-position in 2,6-substituted phenols has been assigned to the group having the greatest effect. Thus in the compound commonly called 2,4-dimethyl-6-*tert*-butylphenol, the more effective *tert*-butyl group is assigned the 2-position. Where a methyl group and another group have the same effect, the methyl group is assigned the 2-position.

The method of calculation is illustrated by calculating the relative molar potency of 2,4-dimethyl-6-isobutylphenol at a concentration of 100 p.p.m.

$$A = \text{2-methyl} = 3.0 + 0.5 \log c$$

$$B = \text{4-methyl} = 10.5 - 2.0 \log c$$

$$C = \text{6-isobutyl} = 5.0 - 0.5 \log c$$

$$A + B + C = 18.5 - 2.0 \log c$$

$$\text{Relative molar potency} = (A + B + C)2^{2-H-R+HR}$$

$$(18.5 - 2.0 \log 100)2^{2-0-0+0} = (18.5 - 4.0)2^2 = 58.0$$

Table V shows the results of calculating relative molar potencies for 37 phenols. The deviation from the observed value in the range of 100 to 1000 p.p.m. is in the range of ±1.85 to ±2.47.

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