ACKNOWLEDGMENT

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Sulfur Compounds as Antioxidants

BETA-ALKYLMERCAPTOKETONES

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 ${f T}_{f his}$ study was made for the purpose of finding new antioxidants.

It was discovered that certain types of sulfur-containing compounds are antioxidants. These compounds may be classified as β -alkylmercaptoketones and have the follow-

ing general formula:
$$R-S-C-C-R'$$
. They may be

prepared readily by the addition of mercaptans to α,β unsaturated ketones in the presence of acidic or basic catalysts. The most effective inhibitors were synthesized from di- α , β -unsaturated ketones with primary alkylmercaptans.

A new type of inhibitor to retard autoxidation of organic materials has been developed. These compounds are very different from the usual aromatic amino or hydroxy compounds.

N THE study of oxidation inhibitors for use in fats and oils a new class of compounds which are effective antioxidants has been found (9). These materials constitute a radical departure from the usual inhibitors that comprise hydroxy and/or amino aromatics.

These new inhibitors are β -alkylmercaptoketones all containing R'R'''O

the group RSCCC-R'''', where the R's represent hydrogen or R''H

organic radicals of the type of alkyl, aryl, or heterocycle. Representative compounds of this class are listed in Tables I to III. In general, all these compounds are antioxidants in lard, but they are not all of equivalent effectiveness. This paper reports the results of work intended to investigate the features of β -alkylmercaptoketones that lead to high potency as antioxidants.

 β -Alkylmercaptoketones are readily prepared by the addition of mercaptans to α,β -unsaturated ketones using either acid or basic catalysts.

$$\begin{array}{c} \mathbf{R}' \mathbf{R}''' \mathbf{R}''' & \mathbf{R}''' \mathbf{R}''' \\ | & | & | \\ \mathbf{C} = \mathbf{C} - \mathbf{C} = \mathbf{0} + \mathbf{RSH} \longrightarrow \mathbf{RSC} \quad \mathbf{CHC} = \mathbf{0} \\ \mathbf{R}'' & \mathbf{R}'' \end{array}$$
(1)

Posner (θ) carried out a large number of additions of mercaptans to α,β -unsaturated ketones. However, usually he did not isolate the primary addition product but preferred to oxidize it to the corresponding sulfone, ordinarily a crystalline substance which can easily be isolated. Posner's reactions were carried out using anhydrous hydrogen chloride as a catalyst; this acid type catalyst promotes addition, at the β -carbon atom, of a mercapto residue as well as reaction at the carbonyl group to form dithioacetals.

$$\begin{array}{ccc} R' & R''' R'''' \\ C = CC = O + 3RSH \xrightarrow{\text{Acid}} RSC - CHC (SR)_2 + H_2O \quad (2) \\ R'' & R'' \end{array}$$

However, in some instances, dithioacetals are not formed, and the only reaction product is the one that results from addition of the mercaptan across the double bond according to Equation 1. Ruheman (8) repeated much of Posner's work using basic catalysts which do not cause the formation of the dithioacetals but give reactions only of the type of Equation 1. Later Nicolet (5) was able to carry out some of the reactions of Equation 1 without any catalyst by heating the mixture of reactants to the temperature of a steam bath for short intervals of time.

The addition of mercaptans to α,β -unsaturated ketones does not proceed with equal facility in all cases but depends on the nature of the ketone and the mercaptan. Thus ketones with two hydrogen atoms on the β -carbon atom add mercaptans most readily, those with only one hydrogen atom with more difficulty, and those with no hydrogen atoms least readily. Of the mercaptans those with long chains (10 or more carbons) are relatively sluggish and do not react readily. The primary mercaptans add much more easily than the tertiary. Mercaptans that have polar groups-for example, thiocresol, mercaptoethanol, thioglycolic acid, and thioglycerol-add most readily.

Various ketones and mercaptans were employed as reactants to prepare β -alkylmercaptoketones. The potency of the products as antioxidants was determined using the Swift active oxygen method (A.O.M.) (3). In these tests lard was used as the substrate for testing purposes. Preliminary tests on a compound of this type indicate a low order of toxicity. Potency as antioxidant was found to depend on the nature both of the mercaptan and of the ketone.

Table I, wherein products obtained from the reaction of mercaptans with mono- α,β -unsaturated ketones are shown, demonstrates the effect of varying the nature of the mercaptan on potency. Thus the products obtained by adding thiocresol or tert-butyl mercaptan to benzalacetophenone (compounds 3) and 4) are less effective as compared to the one prepared with chiefly primary mercaptans (compound 9). The same result is

. . .

	Compound	Formula	Melting Point, °C.	Boiling Point, °C.	Stability Time, Hours
1.	7.8-Dihydroxy-5-thia-2-octanone	CH2CHCH2SCH2CH2COCH3	٩	a	50-66 ^b
		он он			
2.	4-Phenyl-4-ethylmercapto-2-butanone	C ₆ H ₆ CHCH ₂ COCH ₃ SC ₂ H ₅	10	962.0 mm.	48-66 ^b
3.	ω -Phenyl- ω -tert-butylmercaptopropio- phenone	C6H6CHCH3COC6H5 SC(CH3)3	80-81	•••••	<16 b
4.	ω-Phenyl-ω-(4-methylphenylmercapto) propiophenone	$C_6H_6CHCH_2COC_6H_5$ $SC_6H_4CH_3-p$	113-114	• • • • •	<18 ^b
5.	4-Phenyl-4-p-methylphenylmercapto-2- butanone	p-CH ₂ C ₆ H ₄ SCHCH ₂ COCH ₈ \downarrow C ₆ H ₅	63-64	•••••	110
6.	4-Methyl-4-p-methylphenylmercapto- 2-pentanone	$p-CH_{2}C_{6}H_{4}SCCH_{2}COCH_{2}$ (CH ₂) ₂	.21	•••••	15¢
7.	4-Alkylmercapto-2-butanone	$R'SCH_2CH_2COCH_8^d$		91-9615 mm.	38 *
8.	4-Methyl-4-ethylmercapto-2-pentanone	C2H6SCCH2COCH3 (CH3)2	• • • • •	45-503 mm.	2534 °
9.	ω-Phenyl-ω-alkylmercaptopropiophe- none	C6H5CH—CH2COC6H5d SR'	36-40		67-73 °
	 ^a Could not be distilled or crystallized to ^b 0.02% by weight in 4¹/₂-hour lard. ^c 0.10% by weight in 9-hour lard. ^d R' is chiefly n-propyl obtained from sou ^e 0.02% by weight in 9-hour lard. 	get analytically pure sample. Ir gasoline.			

TABLE I. MONO- α,β -UNSATURATED KETONES PLUS MERCAPTANS

shown in a comparison of 4-methyl-4-*p*-methylphenylmercapto-2-pentanone and 4-methyl-4-ethylmercapto-2-pentanone (compounds 6 and 8), the latter being the more effective of the two.

In Table II the products that have been prepared by adding mercaptans to some linear di- α , β -unsaturated ketones are listed. It is possible to add either 1 or 2 moles of mercaptan to di- α , β unsaturated ketones. For example, phorone reacts with ethyl mercaptan in the presence of piperidine as a catalyst to give chiefly addition of 1 mole of mercaptan, whereas with hydrogen chloride as a catalyst the chief product contains 2 moles of mercaptan.



Tert-butyl mercaptan, which is more sluggish than ethyl mercaptan, requires more drastic conditions to effect reaction with phorone than does the primary mercaptan. Only one molecule of the *tert*-alkyl mercaptan adds to dibenzalacetone; in this respect it is similar to sulfinic acids only one molecule of which adds to dibenzalacetone (4).

As a whole the compounds prepared from the di- unsaturated ketones are more potent than those from the mono- unsaturated. Again the same less effective inhibitors result in those products prepared from *tert*-alkyl or aromatic mercaptans (compounds 10 and 14).

One other group of compounds has been prepared which belongs to this class (Table III). This group, discussed separately because the results show the effect of varying the nature of the ketone and are not in accord with those already reported, includes 3-ketotetrahydrothiophene and the products obtained by adding mercaptans to α, α' -dibenzal cyclic ketones. 3-Ketotetrahydrothiophene (10) should be an inhibitor, since it contains a sulfur β to the keto group. Condensation of 2,4-dibenzalketotetrahydrothiophene with two molecules of mercaptan should give an inhibitor. In Table III the products prepared from ketotetrahydrothiophene as well as from cyclopentanone and cyclohexanone are shown.

2,4 - Dibenzal - 3 - ketotetrahydrothiophene adds only one molecule of ethyl mercaptan under the same conditions that 2,6-dibenzalcyclohexanoneadds two; likewise addition of two molecules of ethyl mercaptan to 2,5-dibenzalcyclopentanone is more difficult than to the homologous cyclohexanone. As shown in the table the products derived from ketotetrahydrothiophene are less effective inhibitors (compounds 19, 20, and 21). In keeping with this fact, the product prepared from cyclopentanone is also less effective (compound 22). However, the compound which contains a cyclohexanone ring is a more effective inhibitor (compound 23).

In an attempt to explain the results obtained with the cyclic ketones, models were constructed. These models clearly

show that in 3-ketotetrahydrothiophene the sulfur and keto groups are held rigidly apart by the planar ring. In the 2,5-bis(α ethylmercaptobenzyl)cyclopentanone, because of the planar configuration of the five-membered ring, close approximation of the keto and sulfur groups is hindered; the same condition prevails with 2-(a-ethylmercaptobenzyl)-4-benzal-3-ketotetrahydrothiophene. However, in 2,6-bis(α -ethylmercaptobenzyl)cyclohexanone these two groups can attain a close approximation because of the flexibility of the six-membered ring. It appears that some type of specific steric arrangement, possibly quasiring formation, involving close approach of the sulfur and the oxygen of the keto groups, is necessary in order to have a more effective inhibitor. There does not appear to be any other explanation for all of the facts of (1) lower potency of some cyclic ketones and (2) lower potency of compounds derived from tertalkyl and aromatic mercaptans. Thus the bulky tert-butyl group may also offer steric hindrance to the proper spacial arrangement of the molecule necessary in a more effective inhibitor. In materials made with aromatic mercaptans steric hindrance does not appear to be a valid explanation for lower potency; it is conceivable that the free electrons on sulfur are too much involved in resonance with the nucleus to participate in any sort of ring formation that may be necessary.

In order to learn more about the importance of steric relationships an attempt was made to prepare the diphenyltetrahydrothiopyrone (I) by the reaction of 1 mole of hydrogen sulfide with 1 mole of dibenzalacetone to yield I



which would have sulfur β to the carbonyl on both sides, unlike 3-ketotetrahydrothiophene; but because of the ring, close approximation of the keto and sulfur is prevented. On

	Compound	Formula	Melting Point, °C.	Boiling Point, °C.	A.O.M. Stability Time, Hours
10.	1,5-Diphenyl-2- <i>tert</i> -butylmercapto-4- penten-3-one	$C_6H_4CH = CHCOCH_2CH \cdot C_6H_6$ \downarrow $SC(CH_4)_8$	99–101		<19ª
11.	2,6-Dimethyl-2,6-diethylmercapto-4- heptanone	$\begin{bmatrix} C_2H_{4}SC \\ -CH_{3}\\CH_{4}\end{bmatrix}_{2}CO$		102-1058.0 mm.	$71-76^{a}\ 105^{b}\ 63^{c}$
12.	1,5-Diphenyl-1,5-diethylmercapto-3- pentanone	$\begin{bmatrix} C_6H_5CHCH_2\\ SC_2H_5 \end{bmatrix}_2^{CO}$	33-35		49-66ª
13.	5,9-Diphenyl-1,2,12,13-tetrahydroxy- 4,10-dithiatridecan-7-one	$\begin{bmatrix} C_{6}H_{3}CHCH_{2} \\ I \\ SCH_{2}CHCH_{2} \\ OH \\ OH \\ OH \end{bmatrix}_{2}^{CO}$	đ		28-30 ^a
14.	1,5-Diphenyl-1,5-bis-(4-methylphenyl- mercapto)-3-pentanone	$\begin{bmatrix} C_{6}H_{5}CHCH_{2}\\ SC_{6}H_{4}CH_{3}-p \end{bmatrix}_{2}^{CO}$	90-91	•••••	<18ª
15.	2,6-Dimethyl-2-ethylmercapto-5- hepten-4-one	$\begin{array}{c} C_2H_{\mathfrak{s}}SCCH_{\mathfrak{s}}COCH = C(CH_{\mathfrak{s}})_2 \\ (CH_{\mathfrak{s}})_2 \end{array}$	••••	81- 833.0 mm.	59-636
16.	2,6-Dimethyl-2,6-bis-(carboxymethyl- mercapto)-4-heptanone	$\begin{bmatrix} (CH_3)_2C-CH\\ \downarrow\\ SCH_2CO_2H \end{bmatrix}_2^CO$	113-115	•••••	83-89 ⁵
17.	2,6-Dimethyl-2,6-bis-(β-bydroxyethyl- mercapto)-4-heptanone	$\begin{bmatrix} (CH_3)_2CCH_2 \\ I \\ SCH_2CH_2OH \end{bmatrix}_2^{CO}$	• • • • •	140-1451.0 mm.	76-90 ^b
18.	1,5-Diphenyl-1,5-di(alkylmercapto)-3- pentanone	$\begin{bmatrix} C_6H_6CHCH_2 \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	•••••	•••••	67-735
 0.02% by weight in 4^{1/2}-hour lard. 0.02% by weight in 9-hour lard. 0.01% by weight in 9-hour lard. Could not be distilled or crystallized to get analytically pure sample. R' is chiefly n-propyl obtained from sour gasoline. 					

TABLE II, DI- α , β -UNSATURATED KETONES PLUS MERCAPTANS

TABLE III. CYCLIC &-THIOKETONES

	Compound	Formula	Melting Point, °C.	Boiling Point, °C.	A.O.M. Stability Time, Hours
19.	3-Ketotetrahydrothiophene	CH ₂ —CO CH ₂ CH ₂		74.5 ₁₅ mm.	<184
20.	3-Keto-4-carbomethoxytetrahydro- thiophene	CH ₂ O ₂ CCH ₂ CH—CO CH ₂ CH ₂ CH ₂ S	•••	128.5 ₃₀ mm.	<18ª
21	2-(α-Ethylmercaptobenzyl)-4- benzal-3-ketotetrahydrothio- phene ^δ	$C_{6}H_{5}CH = C - CO$ $C_{1}CH_{2}CH - C - C_{6}H_{5}$ S $SC_{2}H_{5}$	63-67	•••••	<19ª
22	2,5-Bis(a-ethylmercaptobenzyl)- cyclopentanone	$\begin{array}{c} CO\\ C_6H_5CHCH\\ SC_2H_5\\ CH_2CH_2\\ CH_2CH_2\\ SC_2H_5\\ CH_2CH_2\\ CH_2CH_2\\$	58-59		<21ª
23	2.6-Bis-(α-ethylmercaptobenzyl)- cyclohexanone	$\begin{array}{c} CO\\ C_{e}H_{e}CHHO\\ SC_{s}H_{6}\\ CH_{2}\\ CH_{2}\\ CH_{2}\\ CH_{2}\\ CH_{2}\\ \end{array}$	88-89		48 ¢

^a 0.02% by weight in 4¹/₂-hour lard. ^b May also contain or be 4-*a*-ethylthiobenzyl-2-benzal-3-ketotetrahydrothiophene or mixtures of these two materials.

TABLE IV. *a*, *b*-Olefinic Systems Plus Mercaptans

	Compound	Formula	Melting Point, °C.	Boiling Point, °C.	A.O.M. Stability Time, Hours	
24.	1-Phenyl-1-alkylmercapto-2-nitroethane	C6H5CHCH2NO2	•••	111-112 ₁₁ mm.	13-200	
25.	1-Phenyl-1-tert-butylmercapto-2-nitroethane	C6H5CHCH2NO2	64-65		20 b	
26.	β -(carbomethoxymethylmercapto)propionitrile	CH2SCH2CH2CN CO2CH1	•••	1032.0 mm.	< 18 ^b	
^a R' is chiefly n-propyl obtained from sour gasoline. • 0.02% by weight in 9-hour lard.						

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carrying out this reaction the expected cyclic compound was not obtained but instead a thermoplastic resin which presumably is II.

C6H5CHCH2COCH2CHC6H5 (\mathbf{II})

Formation of a linear polymer rather than a six-membered cyclic monomer has been reported for divinyl sulfone with compounds that contain two active hydrogens such as nitroparaffins (1). Dibenzalacetone may be regarded as an analog of divinyl sulfone, and hydrogen sulfide contains two active hydrogens.

Further consideration of the source of antioxidant activity in these materials led to additional experiments. Oxidation of 2,6-dimethyl-2,6-diethylmercapto-4-heptanone(7) to the corresponding sulfone (III) gives a product which is completely inactive as an inhibitor in lard.

 $(CH_8)_2 C CH_2 CH_2 CO$ $SC_{2}H_{5}$ $\begin{bmatrix} (CH_3)_2 C CH_2 \\ O_2 SC_2 H_5 \end{bmatrix}_2^{CO} (III)$

It appears, therefore, that the presence of a divalent sulfur is essential to obtain effective inhibitors.

According to the patent literature (\mathcal{Z}) β -thioaliphatic acids, 0

RSCH₂CH₂C-OH, are also antioxidants for lard, Since the keto and carboxyl group differ markedly in many respects, mercaptans have been added to two other systems which contain an olefinic group conjugated with a different unsaturated group. These systems comprise ω -nitrostyrene and acrylonitrile. The nitro and nitrile groups are greatly different from the keto group, but systems $C=CNO_2$ and C=C-C=N react similarly to C=C-C=O in many 1,4-addition reactions, and it seemed possible that the products formed by condensation of such systems with mercaptans might be inhibitors. The compounds July 1951

of this type shown in Table IV are indifferent inhibitors. It appears, therefore, that the keto group cannot necessarily be replaced with analogous groups and that the keto group has some function rather than merely acting as an activator for addition of the mercaptan since the nitro and cyano groups also fulfill this function.

EXPERIMENTAL

There is a large amount of literature available on the addition of mercaptans to α,β -unsaturated ketones; detailed experimental directions are not given for all of the compounds prepared.

CONDENSATION WITH AN ACID CATALYST. With those ketones which are liquid the mixture of ketone and mercaptan is cooled in an ice bath and saturated with anhydrous hydrogen chloride. If the ketone is a solid, a homogeneous solution can be obtained by using a small amount of acetic acid as a solvent; the solution is then saturated with hydrogen chloride as described.

The acid solution is allowed to stand at room temperature for 5 to 7 days (this long a time is unnecessary in many instances) and then poured into water. The organic material is extracted with a solvent as petroleum ether or benzene, washed several times with water, and finally with bicarbonate to remove all the acid. After evaporation of the solvent, the residue may be crystallized or distilled in vacuo as is suitable. CONDENSATION WITH BASIC CATALYST. Although piperidine was used in the majority of condensations in this work, Triton B. (benerylty included) or honorylty but holds and the base of the solvent by a substantial sector.

CONDENSATION WITH BASIC CATALYST. Although piperidine was used in the majority of condensations in this work, Triton B (benzyltrimethylammonium hydroxide) or benzyltrimethylammonium butoxide (both from Rohm & Haas Co., special products department) is more effective. In general it is more convenient to use a basic instead of an acid catalyst. The catalyst, a few drops, is added to the mixture of ketone and mercaptan. Frequently heat is liberated but some gentle heating may be desirable. If a solvent is necessary, ethyl acetate is satisfactory. After brief standing or heating the reaction mixture is dissolved in petroleum ether or ethyl acetate, washed with 0.5% sulfuric acid to remove all catalyst, and the solvent is evaporated. The residue may be suitably crystallized or distilled.

SUMMARY

 β -Alkylmercaptoketones have been found to be antioxidants in lard. The best of these compounds are obtained by adding primary mercaptans to di- α , β -unsaturated ketones. Potent inhibitors result from addition of primary mercaptans to mono- α , β -unsaturated ketones. Addition of tertiary or aromatic mercaptans to either class of unsaturated ketones yields products which are less effective inhibitors.

Study of some cyclic β -alkylmercaptoketones suggests that in the less effective inhibitors close approximation of the keto oxygen and the sulfur is hindered. In the more effective antioxidants close approximation can be easily achieved.

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VISCOSITY BEHAVIOR OF GASES

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The need has existed for a review of methods for prediction of gas viscosity including effects of pressure, temperature, and composition, and for presentation of these methods in convenient form for engineering use.

Charts are presented for prediction of the effect of temperature at low pressures based on the refined kinetic theory of Chapman and Cowling as developed by Hirschfelder, Bird, and Spotz. Required constants are tabulated for the common gases and methods for estimation of unknown values are presented. Detailed tables of temperature functions are given for use when high accuracy is necessary. Graphs based on the work of Uyehara and Wat-

NOWLEDGE of gas viscosity is essential in many problems of fluid flow, heat and mass transfer. The rigorous kinetic theory of viscosity is extremely complex and many of the equations presently available in the literature are not in most convenient form for numerical calculations. In the present paper some of the most useful relations for viscosity behavior are summarized and presented in simplified form for engineering use.

Recently, Hirschfelder, Bird, and Spotz (8) have published tables of collision integrals based on the refined kinetic theory of Chapman and Cowling (3) which permits accurate calculation of son have been constructed for estimation of effects of pressure and temperature on viscosity of gases at high pressures. Constants for gas mixture viscosity equations are presented in graphical form to simplify the calculation of viscosity in multicomponent systems. Methods for prediction of gas viscosity are reviewed and compared.

It is believed that this work will be of use in engineering where knowledge of viscosity of gases or gas mixtures is required. The charts and simplified equations which are presented should materially reduce numerical calculations ordinarily required, and yet yield results which are sufficiently precise for most purposes.

viscosity for nonpolar smooth spherical molecules. This treatment assumes the form given by Equation 1 for the energy of interaction potential between two molecules.

$$E(r) = 4\epsilon \left[-\left(\frac{r_o}{r}\right)^6 + \left(\frac{r_o}{r}\right)^{12} \right]$$
(1)

where E(r) = energy of interaction

 ϵ = energy difference between the separated molecules and the molecules in the configuration in which they have the maximum energy of attraction ergs