Addition of Alkanedithiols to Olefins

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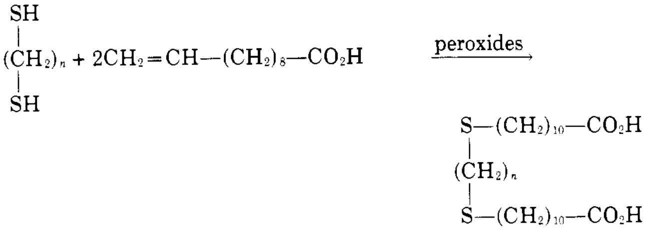
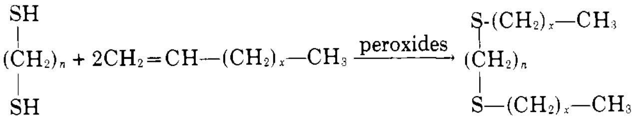
A series of α,ω-dithioalkylalkanes was synthesized from alkanedithiols and terminal olefins under free radical conditions. The alkanedithiols employed were: 1,2-ethane-, 1,3-propane-, 1,4-butane- and 1,5-pentanedithiol. The olefins employed were: 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene and 1-octadecene. Structures of these compounds were confirmed by treating the appropriate n-alkyl bromides with the sodium salts of the corresponding alkanedithiols. The α,ω-dithioalkylalkanes were oxidized to the corresponding disulfones by hydrogen peroxide.

RECENTLY (*1*) it was shown that 1 mole of alkanedithiol adds to 2 moles of 10-undecenoic acid under free radical conditions to form alkane bis-(11-mercaptoundecanoic) acids.



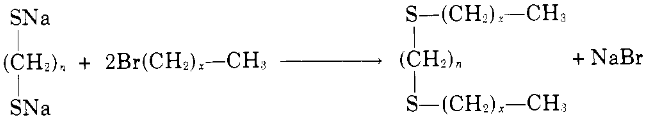
$$\begin{array}{l}\text{SH}\\ |\\ (\text{CH}_2)_n\\ |\\ \text{SH}\end{array} + 2\text{CH}_2{=}\text{CH}{-}(\text{CH}_2)_8{-}\text{CO}_2\text{H} \xrightarrow{\text{peroxides}} \begin{array}{l}\text{S}{-}(\text{CH}_2)_{10}{-}\text{CO}_2\text{H}\\ |\\ (\text{CH}_2)_n\\ |\\ \text{S}{-}(\text{CH}_2)_{10}{-}\text{CO}_2\text{H}\end{array}$$

In this article, the reaction has been extended to other terminal olefins, among which are 1-octadecene, 1-hexadecene, 1-tetradecene, 1-dodecene, and 1-decene.



$$\begin{array}{l}\text{SH}\\ |\\ (\text{CH}_2)_n\\ |\\ \text{SH}\end{array} + 2\text{CH}_2{=}\text{CH}{-}(\text{CH}_2)_x{-}\text{CH}_3 \xrightarrow{\text{peroxides}} \begin{array}{l}\text{S}{-}(\text{CH}_2)_x{-}\text{CH}_3\\ |\\ (\text{CH}_2)_n\\ |\\ \text{S}{-}(\text{CH}_2)_x{-}\text{CH}_3\end{array}$$

The addition takes place to form compounds of anti-Markownikoff configuration with yields ranging between 40 and 60% (Table I). The structures of these compounds were confirmed by forming the α,ω-dithioalkylalkanes by treating the appropriate *n*-alkyl bromides with the sodium salts of the corresponding alkanedithiols.

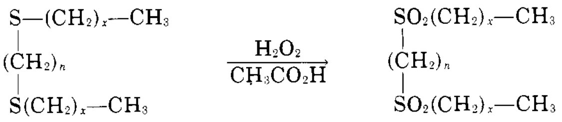


$$\begin{array}{l}\text{SNa}\\ |\\ (\text{CH}_2)_n\\ |\\ \text{SNa}\end{array} + 2\text{Br}(\text{CH}_2)_x{-}\text{CH}_3 \longrightarrow \begin{array}{l}\text{S}{-}(\text{CH}_2)_x{-}\text{CH}_3\\ |\\ (\text{CH}_2)_n\\ |\\ \text{S}{-}(\text{CH}_2)_x{-}\text{CH}_3\end{array} + \text{NaBr}$$

Table I represents the composition and melting point data for both addition compounds and compounds prepared by the reaction of the sodium salt and alkylhalide.

The α,ω-dithioalkylalkanes show an alternation of melting points (Figure 1). In Figure 1 the melting points of α,ω-dithioalkylalkanes are plotted against the number of carbon atoms in the alkanedithiols. The derivatives of 1-decene are lowest melting, while the derivatives of 1-octadecene are highest melting.

The α,ω-dithioalkylalkanes were oxidized to the corresponding disulfones by hydrogen peroxide in glacial acetic acid.



$$\begin{array}{l}\text{S}{-}(\text{CH}_2)_x{-}\text{CH}_3\\ |\\ (\text{CH}_2)_n\\ |\\ \text{S}(\text{CH}_2)_x{-}\text{CH}_3\end{array} \xrightarrow[\text{CH}_3\text{CO}_2\text{H}]{\text{H}_2\text{O}_2} \begin{array}{l}\text{SO}_2(\text{CH}_2)_x{-}\text{CH}_3\\ |\\ (\text{CH}_2)_n\\ |\\ \text{SO}_2(\text{CH}_2)_x{-}\text{CH}_3\end{array}$$

The properties, yields obtained, and analyses of the sulfones are summarized in Table I.

EXPERIMENTAL

All melting points are uncorrected and were determined by the capillary tube method.

1-Octadecene, 1-hexadecene, 1-tetradecene, 1-dodecene, 1-decene, 1-bromooctadecane, 1-bromohexadecane, 1-bromotetradecane, 1-bromododecane, and 1-bromodecane were obtained from Eastman Kodak Co. The alkanedithiols were obtained from Aldrich Chemical Co. The olefins were distilled before use.

α,ω-Dithioalkylalkanes. To 0.04 mole of the 1-alkene in a 100-ml. roundbottomed flask, fitted with a reflux

Table I. Composition and Melting Point

n	*x*	Yield, %	M.P., °C.	Sulfur, % Calcd.	Sulfur, % Found
		α,ω-Dithioalkylalkanes			
2	9	47	44–45	17.1	17.4
3	9	46	38–39	16.5	16.7
4	9	55	41–42	15.9	16.0
5	9	40	41–42	15.4	15.4
2	11	42	54–55	14.9	14.7
3	11	50	46–47	14.4	14.2
4	11	48	51–52	14.0	13.9
5	11	41	54–55	13.6	13.3
2	13	46	62–63	13.2	13.0
3	13	52	56–57	12.8	13.1
4	13	51	59–61	12.4	12.2
5	13	50	61–62	12.2	12.3
2	15	40	68–69	11.8	11.9
3	15	49	61–62	11.5	11.6
4	15	51	64–65	11.2	11.2
5	15	40	76–77	11.0	11.1
2	17	43	70–71	10.7	10.8
3	17	63	68–69	10.5	10.5
4	17	40	71–72	10.2	10.4
5	17	56	76–77	10.0	10.3
		Sulfones			
2	9	85	164–165	14.6	14.4
3	9	97	166–167	14.2	14.2
4	9	95	152–153	13.7	13.7
5	9	93	139–140	13.3	13.3
2	11	96	161–162	13.0	12.9
3	11	95	161–162	12.6	12.5
4	11	87	149–150	12.3	12.3
5	11	86	134–135	11.9	12.1
2	13	87	141–142	11.6	11.8
3	13	92	154–155	11.3	11.2
4	13	84	142–143	11.1	11.1
5	13	81	132–133	10.8	10.9
2	15	90	143–144	10.5	10.3
3	15	88	158–159	10.3	10.5
4	15	90	143–144	10.1	10.2
5	15	97	130–131	9.9	9.6
2	17	81	140–141	9.7	9.8
3	17	96	156–157	9.5	9.7
4	17	80	142–143	9.3	9.2
5	17	94	134–135	9.1	9.3

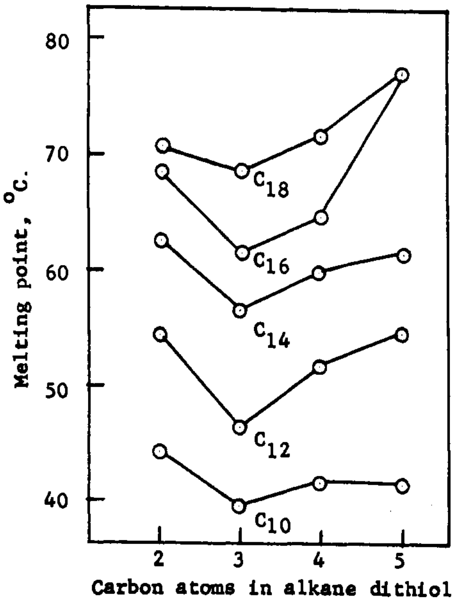


Figure 1. Melting points of α, ω-dithioalkylalkanes vs. the number of carbon atoms in the alkanedithiols

condenser, were added 50 ml. of benzene, 0.02 mole of the appropriate alkanedithiol, and 0.2 gram of benzoyl peroxide. The reaction mixture was then heated under gentle reflux on a steam bath for 5 hours. At the end of this time, the benzene was removed by distillation and the resulting solid was crystallized from acetone or acetone-alcohol. The white solid was then chromatographed with Florisil and eluted with benzene. After removal of the benzene by distillation, the compound was again crystallized from acetone or acetone-alcohol.

ALTERNATE PREPARATION. To 0.022 mole of the appropriate alkane dithiol in a 500-ml. round-bottomed flask, fitted with a reflux condenser and a calcium chloride drying tube, were added 300 ml. of dry dioxane and 0.92 gram (0.04 gram-atom) of sodium. The mixture was heated under gentle reflux for 72 hours or until all of the sodium had been consumed. To the resulting suspension was added 0.04 mole of the appropriate 1-bromoalkane dissolved in 100 ml. of dry dioxane and the mixture was heated under gently reflux for 72 hours. The mixture was then poured into 300 ml. of water and the solid which formed was separated by filtration and washed with three 50-ml. portions of water. The product was then purified as above.

OXIDATION. To 0.011 mole of the α,ω-dithioalkylalkane in a 125-ml. Erlenmeyer flask was added 25 ml. of glacial acetic acid and the flask was chilled in an ice bath. To the flask was added 0.26 mole of 30% hydrogen peroxide and the mixture was allowed to stand in the melting ice bath for 72 hours. The resulting solid was separated by filtration and crystallized from acetone until successive crystallizations showed no increase in melting point. The results are summarized in Table I.

LITERATURE CITED

(1) Sasin, G.S., Longo, F.R., Berger, R., DeSantis, W., Sasin, R. *J. Org. Chem.* **26**, 3538 (1961).

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New Acyloxysilanes and Their Reaction with Grignard Reagents

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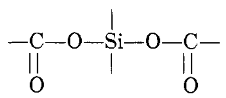
Tetra(2,4-dichlorophenoxyacetoxy)silane, tetra(α-naphthylacetoxy)silane and tetra(2,2-dichloropropionoxy)silane have been prepared by the reaction of tetrachlorosilane with the sodium salts of the acids. The infrared spectra of these acyloxysilanes have been determined between 3 and 15 microns. 2,4-Dichlorophenoxymethyl ethyl ketone and a silicone have been prepared by action of ethylmagnesium bromide on tetra(2,4-dichlorophenoxyacetoxy)silane. The infrared spectrum of the ketone was determined between 3 and 15 microns. In the same way, a ketone and a silicone were produced from tetra(α-naphthylacetoxy)silane. Acetone and chloroform have been found to be good reaction mediums for the preparation of acyloxysilanes.

THE METHOD of preparing acyloxysilanes from tetrachlorosilane and sodium salts of organic acids has been used by Schuyten, Weaver, and Reid (*11*) to prepare tetraacetoxysilane, by Lanning (*7, 8*) to prepare tetrapropionoxysilane and tetrabenzoxysilane, and by Lanning and Moore (*9*) to prepare a series of more complicated acyloxysilanes. The method has now been applied to the preparation of tetra(2,4-dichlorophenoxyacetoxy)silane, tetra(α-naphthylacetoxy)silane and tetra(2,2-dichloropropionoxy)silane in from 55.9 to 63.3% yields (Table I).

Like other acyloxysilanes (*4, 7*) these white solid compounds react with alcohol and water. They decompose when heated.

Infrared spectra of these compounds were determined between 3 and 15 microns. The spectra for tetra(2,4-dichlorophenoxyacetoxy)silane, tetra(α-naphthylacetoxy)silane and tetra(2,2-dichloropropionoxy)silane are given in Figures 1, 2, and 3.

All three acyloxysilanes show significant absorption bands near 9.2, 5.8, and 10.8 microns. The 9.2 band corresponds to values reported by Richards and Thompson (*10*) to be characteristic of the Si—O bond. The 5.8 micron band is due to the C=O bond, and the ones near 10.8 microns are probably due to the



$$-\underset{\overset{\|}{O}}{C}-O-\overset{|}{\underset{|}{Si}}-O-\underset{\overset{\|}{O}}{C}-$$

structure as pointed out by Lanning and Moore (*9*).