methylhydrocinnamylammonium hydroxide,[9] are known to furnish principally propenylbenzene and not more than traces of allylbenzene.

In view of the known capacity of strong alkali in causing the isomerization of allylbenzene to propenylbenzene,[10] it seemed probable that the formation of the latter in the thermal decomposition of trimethylcinnamylammonium hydroxide is a consequence of the strongly alkaline nature of the material. If so, the thermal decomposition of neutral salts of this base would be expected to form allylbenzene. This was realized for both the bromide and the iodide. The acetate decomposed smoothly at 275° but the product, formed in good yield, was dimethylhydrocinnamylamine. The bromide decomposition was used in the dehydration of the deuterated hydrocinnamyl alcohol.

Preparation and Thermal Decomposition of Trimethylhydrocinnamylammonium bromide-*d*.—The alcohol, 14.1 g., was first converted to hydrocinnamyl bromide-*d* (yield, 18.9 g.) by treatment with hydrobromic acid.[11] This product was heated under reflux for six hours with 10.8 g. of trimethylamine in 100 ml. of absolute ethanol. Concentration of the resulting solution caused separation of the quaternary bromide (17.3 g.) as colorless crystalline plates, m.p. 150.5–152°. Without further purification, 15.8 g. of this material was heated in a distilling flask at 280–320°. An ether extract of the distillate, which consisted of liquid hydrocarbon and solid trimethylamine hydrobromide, was washed successively with water, dilute hydrochloric acid, sodium bicarbonate solution and again with water, and was then subjected to fractional distillation. The allylbenzene was collected in two fractions, 3.20 g. in the range 156–158°, $n^{20}\mathrm{D}$ 1.5104, and 0.70 g. in the range 158–160°, $n^{20}\mathrm{D}$ 1.5176 (lit.[10a] $n^{20}\mathrm{D}$ 1.5143), which together constitute a yield of 68%. A further fraction, 0.55 g., b.p. 160–167°, $n^{20}\mathrm{D}$ 1.5295, doubtless contained some additional allylbenzene as well as some propenylbenzene ($n^{20}\mathrm{D}$ 1.5492). Analysis of the first fraction for deuterium showed 17.2 mole % C_9H_9D.

Attempted Carbonation of the Product from Cinnamyl Alcohol and Lithium Aluminum Hydride.—A solution containing the product of the interaction of cinnamyl alcohol and lithium aluminum hydride, prepared as described earlier, was treated with carbon dioxide at 35°. No evidence of a reaction was noted, and upon hydrolysis of the mixture hydrocinnamyl alcohol was isolated in substantially the same yield as before. Likewise a solution of the intermediate product in tetrahydrofuran showed no evidence of a reaction when treated with carbon dioxide at 65°.

Reaction with Oxygen.—Solutions containing the product of the reaction of cinnamyl alcohol with lithium aluminum hydride were found to absorb oxygen readily. Highly concentrated preparations, obtained as viscous liquids or glass-like solids upon evaporation of the solvent, fumed and heated strongly upon exposure to air but did not inflame. The nature of the oxidation product was established in the following experiment. A solution was prepared by the addition of 9 g. (0.067 mole) of cinnamyl alcohol to 0.034 mole of lithium aluminum hydride in ethyl ether solution and the resulting suspension was stirred at room temperature (under nitrogen) for two hours, whereupon a clear solution was formed. Upon passing dry air through the solution a white precipitate formed. The passage of air was continued for eight hours. Aqueous sulfuric acid was then added and the organic product was isolated by ether extraction. Upon attempted distillation at 8 mm. pressure evidence of decomposition was noted; the residue was then transferred to a Hickman alembic and the distillation was conducted at 100° and 0.2 mm. pressure. The product, 2.5 g. of a colorless viscous oil, $n^{20}\mathrm{D}$ 1.5451, was identified as 1-phenyl-1,3-propanediol by conversion to the di-*p*-nitrobenzoate,[12] m.p. 110°.

Summary

It is shown that the reduction of cinnamaldehyde to hydrocinnamyl alcohol by lithium aluminum hydride occurs in two stages, of which the first, giving rise to cinnamyl alcohol, is realized exclusively by performing a reversed addition at lowered temperatures. The further reduction of cinnamyl alcohol is a slower reaction which occurs by addition of metal hydride to the double bond, the metal being replaced by hydrogen during the subsequent hydrolysis. This, as well as the location of the carbon–metal bonds, is shown by tracer studies employing deuterium. The intermediate metallo-organic compound is formulated as a lithium aluminate in which the aluminum is bound, with a coördination number of four, to two carbon atoms and two oxygen atoms. The analogous reduction of allyl to propyl alcohol is found to occur only at higher temperatures.

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[9] von Braun, *Ann.*, **382**, 47 (1911).

[10] (a) Tiffeneau, *Compt. rend.*, **139**, 482 (1904); (b) Klages, *Ber.*, **39**, 2590 (1906).

[11] Norris, Watt and Thomas, This Journal, **38**, 1078 (1916).

[12] St. Pfau and Plattner, *Helv. Chim. Acta*, **15**, 1250 (1932).

Chicago, Illinois Received May 5, 1948

[Contribution from the Chemistry Department of the University of Florida]

Dimercaptols of Acetonylacetone

By Edward G. Rietz, Richard D. Chapman and James B. Fernandez

Considerable has been published on the chemistry of the simple mercaptols but relatively little on the dimercaptols of the 2,5-diketones. Posner observed the reaction of ethyl,[1] *i*-amyl,[1] benzyl[2] and phenyl[2] mercaptans on acetonylacetone but he was interested in the sulfones and paid little attention to the mercaptols.

Inasmuch as acetonylacetone is now readily available, it was decided to prepare a series of dimercaptols and to study them more adequately. Accordingly, the methyl, ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl and *n*-dodecyl mercaptols were prepared as well as the mercaptol from thioglycolic acid. All of these compounds, with the exception of the ethyl derivative, are new to the literature. The latter compound was described by Posner as a liquid; we have obtained it as a solid, melting at 27°, although it may be supercooled without difficulty.

All of the compounds were prepared by the interaction of the mercaptan and acetonylacetone at room temperature under the influence of hydro-

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[1] Posner, *Ber.*, **33**, 2983–2993 (1900).

[2] Posner, *ibid.*, **35**, 493–495 (1902).

TABLE I

PROPERTIES AND ANALYSES OF THE MERCAPTOLS, $CH_3C(SR)_2CH_2CH_2C(SR)_2CH_3$

Mercaptol	M. p., °C.	d^{25}_4	$n^{25}D$	*M*D Calcd.	*M*D Found		Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Methyl	75					$C_{10}H_{22}S_4$	44.40	44.48[a]	8.20	8.24
Ethyl	27	1.036	1.5390	98.8	98.5	$C_{14}H_{30}S_4$	51.45	51.80	9.30	9.50
n-Propyl	−9.5	1.000	1.5260	117.2	117.4	$C_{18}H_{38}S_4$	56.50	56.30	9.98	9.60
n-Butyl	−9.0	0.978	1.5151	135.7	135.3	$C_{22}H_{46}S_4$	60.85	60.47	10.56	10.45
n-Hexyl	11.5	0.946	1.5060	172.7	173.0	$C_{30}H_{62}S_4$	65.42	65.20	11.30	10.90
n-Octyl	38					$C_{38}H_{78}S_4$	68.81	68.50	11.85	11.80
n-Decyl	58					$C_{46}H_{94}S_4$	71.24	70.70[b]	12.22	12.62
n-Dodecyl	66					$C_{54}H_{110}S_4$	73.06	72.80[c]	12.41	12.80
HO_2C-CH_2-	166					$C_{14}H_{22}S_8O_8$	37.56	37.20[d]	4.95	4.95

[a] Calcd.: S, 47.40. Found: S, 47.40. [b] Calcd.: S, 16.54. Found: S, 16.89. [c] Calcd.: S, 14.45. Found: S, 14.51. [d] Calcd.: neut. equiv., 111.6., Found: neut. equiv., 112.2.

gen chloride. Yields of crude mercaptols were uniform and approximated 75%.

The decyl and dodecyl mercaptols were crystallized from ether; the others, except the methyl and the thioglycolic acid derivatives from alcohol-ether 1:1. These were crystallized from ethanol and from water, respectively.

The physical properties and analyses are shown in Table I and the melting points are plotted in Fig. 1. The melting point diagram is of the usual pattern with a minimum at propyl and butyl. It is interesting that the lengthening of four alkyl chains produces so nearly the same effect as when there is only one.

Except with the methyl and ethyl compounds, low results were obtained when the method of Sampey, Slagle and Reid[3] was employed to determine the sulfur. This method, proposed for the simple sulfides, consists in the cautious addition of bromine water to a benzene solution of the simple sulfide followed by titration of the liberated hydrogen bromide.

$$R_2S + Br_2 \longrightarrow R_2SBr_2$$
$$R_2SBr_2 + H_2O \longrightarrow R_2SO + 2HBr$$

When a two-fold excess of bromine was used and the reaction allowed to proceed in the dark, more bromine was consumed as shown in Table II. The theoretical quantity was consumed by the propyl derivative, but twice the theoretical quantity by the methyl, indicating conversion to the tetrasulfone in the latter instance. The reaction products resulting from bromine oxidation will be studied in more detail later.

Acknowledgment.—The authors are indebted to Dr. E. Emmet Reid for his advice and to T. K. Todsen, R. W. Ingwalson, A. Brent and T. Wicker for assistance in the analytical phases of this work.

Experimental

TABLE II

APPARENT SULFUR CONTENT DETERMINED BY BROMINE OXIDATION

Mercaptol	Sulfur percentage Found Unmodified	Modified	Calcd.
Methyl	47.3	95.9	47.4
Ethyl	40.2	39.3	39.3
n-Propyl	17.5	33.5	33.5
n-Butyl	17.2	22.6	29.2
n-Hexyl	12.9	17.3	23.2
n-Octyl	10.3	10.2	19.3
n-Decyl	7.9	8.3	16.5
n-Dodecyl	6.6	7.8	14.5

Except for slight variations, each dimercaptol was prepared in the same way, interaction of the mercaptan with the ketone at room temperature followed by crystallization. Yields approximated 60% after the recrystallization and were uniform for all dimercaptols. In view of this, detailed experimental procedure will be presented only for the preparation of the first member of the series, the methyl dimercaptol, 2,2,5,5-tetrathiomethylhexane.

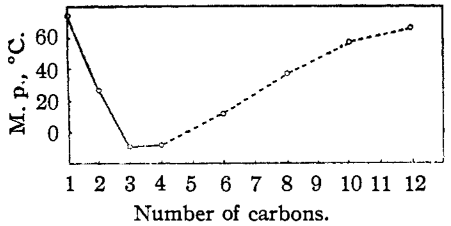

Fig. 1.—Melting points of the mercaptols plotted against the number of carbons in the alkyls.

2,2,5,5-Tetrathiomethylhexane.—Anhydrous hydrogen chloride was passed into 29.0 g. (1/4 mole) of acetonylacetone at −10°. On saturation, 50.0 g. (1 mole) of methyl mercaptan was added and the container stoppered to prevent the escape of the volatile mercaptan. The reaction was permitted to proceed at 0° for two hours whereupon the mixture was permitted to come to room temperature. After twelve hours, the container was opened and the product was recrystallized from hot 95% ethanol. One crystallization yielded pure crystals, m. p. 75°, yield 49.0 g. or 71%.

Summary

1. The acetonylacetone dimercaptols of methyl, ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl mercaptans and thioglycolic acid have been prepared and characterized. All of these, except the ethyl derivative, are new to the literature.

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[3] Sampey, Slagle and Reid, THIS JOURNAL, 54, 3401 (1932).

2. Most dimercaptols do not react normally with bromine water. The methyl and ethyl derivatives react normally but the succeeding members of the homologous series, methyl through dodecyl, fail to react quantitatively.

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[CONTRIBUTION FROM THE DIVISION OF PLANT NUTRITION, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

Starch. I. End-group Determination of Amylose and Amylopectin by Periodate Oxidation

BY A. L. POTTER AND W. Z. HASSID

Hirst, Jones and associates[1] showed that data obtained from periodate oxidation of starch can be utilized for determining the number of glucose residues per non-aldehydic end-group. The values they have obtained for the chain-lengths of a number of starches from different sources and for one sample of crude potato amylopectin were in fair agreement with those obtained by Haworth's methylation end-group method.

This procedure is based on the observation of Jackson and Hudson[2] that when methyl hexopyranosides are attacked by periodate, the ring is disrupted with the elimination of the third carbon atom of the hexose as formic acid. Reducing disaccharides, such as maltose or cellobiose, consisting of two 1,4-linked hexopyranose units, should yield on periodate oxidation one mole of formic acid due to the non-reducing glucose unit and two more moles of this acid due to the reducing glucose residue. Since amylopectin consists of a multitude of branched chains made up of 1,4-linked glucose units, the terminal glucose unit of each chain, like that in the non-reducing end of maltose, contains three hydroxyls on contiguous carbon atoms 2, 3 and 4, and should yield one mole of formic acid on oxidation with periodate. In this polysaccharide the proportion of reducing end-groups is small compared with that of the non-reducing end-groups. Theoretically, only one reducing glucose unit should be present in an undegraded amylopectin molecule, and the formic acid produced from this reducing end-group can thus be ignored. A quantitative determination of the formic acid produced under proper conditions by oxidation of amylopectin with periodate should give a measure of the average chain-length of the branches.

However, formic acid will be liberated from both ends on oxidation of the long straight-chain amylose molecule, the non-reducing glucose unit producing one mole of formic acid, while the reducing glucose unit at the other end will give rise to two moles of formic acid, as shown in Fig. 1. A total of three moles of formic acid should be produced from one mole of amylose.

As pointed out by Halsall, Hirst and Jones,[3] the difficulty of determining end-groups by this method is the fact that polysaccharides, like methylglycosides of reducing disaccharides, have a tendency to be oxidized by periodate beyond the theoretical stage. However, when there is no large excess of sodium periodate present, the rate of production of formic acid is much slower after the theoretical amount has been liberated. Using potassium periodate, which is only slightly soluble in water, and keeping the concentration of formic acid low Hirst, *et al.*,[1,4] obtained satisfactory end-group determinations for amylopectin and glycogen. However, the lowering of concentration of the periodate ion results in a considerable reduction of the rate of reaction. About one-hundred eighty hours at 15° was required to liberate quantitatively the formic acid from the terminal glucose residues in starch.

The purpose of this work was to find conditions which would overcome the difficulty due to over-oxidation and that would lead to an accurate method for estimating the end-groups in amylose and amylopectin. Since only the terminal non-reducing and the reducing glucose units are involved in the actual determination with periodate, the amylose (Fig. 1) can be regarded as a maltose molecule in which the reducing and non-reducing units are united by a long chain of 1,4-linked glucose residues. If conditions for oxidation of maltose to give three moles of formic acid could be established, it would be reasonable to assume that these conditions could also be applied to the determination of end-groups in amylose and amylopectin. Conditions that satisfy this requirement were found when maltose was oxidized with sodium metaperiodate at 2°. The formation of formic acid at first proceeds at a comparatively rapid rate and after three moles of this acid have been liberated, there is a marked decline in rate, as shown in Fig. 2. A similar rate of oxidation was obtained for various amyloses. The point of inflection, which occurs at about twenty-five hours at 2°, is taken as the end-point. However, it is observed that after the primary

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[1] F. Brown, Sonia Dunstan, T. G. Halsall, E. L. Hirst and J. K. N. Jones, *Nature*, **156**, 785 (1945).

[2] E. L. Jackson and C. S. Hudson, THIS JOURNAL, **58**, 378 (1936); **59**, 994 (1937).

[3] T. G. Halsall, E. L. Hirst and J. K. N. Jones, *J. Chem. Soc.*, 1427 (1947).

[4] T. G. Halsall, E. L. Hirst and J. K. N. Jones, *ibid.*, 1399 (1947).