sodium cyanide. Distillation *in vacuo* gave a colorless distillate boiling at 124–140° (3 mm.). Redistillation gave 10.4 to 13 g. (48 to 55% of the theoretical amount) of product boiling at 129–130° (2 mm.); d^{20}_4 1.082; n^{20}_D 1.4570; M_D calcd. 63.11; M_D found 63.68.

Anal. Calcd. for $C_{13}H_{19}O_4N$: C, 61.65; H, 7.51; N, 5.54. Found: C, 61.50; H, 7.46; N, 5.82.

trans-1,2-Cyclohexanedicarboxylic Acid.—Eight grams of ethyl 1-cyano-1,2-cyclohexanedicarboxylate was refluxed with 40 cc. of 20% hydrochloric acid for thirty hours. The ester dissolved and 5.4 g. of colorless acid, melting at 180–184°, separated from the solution. This crude acid gave a neutral equivalent of 86.5 and therefore appeared to be a mixture of the *cis* (m. p. 190°) and the *trans* (m. p. 221°) forms of 1,2-cyclohexanedicarboxylic acid. Heating the crude acid to 160° with 2 cc. of concentrated hydrochloric acid in a sealed tube for two hours converted it into the pure *trans* acid, melting at 221° as described by Baeyer.[6] A mixture of this acid with an authentic sample of *trans*-hexahydrophthalic acid also melted at 221°.

Summary

The cyano ester ring closure has been extended to five- and six-membered rings.

URBANA, ILLINOIS RECEIVED MARCH 21, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Action of Selenium Tetrachloride on Some Esters of Salicylic Acid[1]

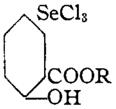
BY R. E. NELSON, ED. F. DEGERING AND JOHN A. BILDERBACK

The action of selenium oxychloride on paraffins, olefins, ethers, ketones, salicylic acid and its esters, amines, and phenols has been described more or less thoroughly in the literature.[2] The question concerning the action of the monochloride and the tetrachloride aroused our interest.

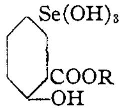
Selenium tetrachloride, according to our study, is a valuable reagent to use in the preparation of organo-selenium compounds. No selenium dioxide or free selenium is produced in this reaction. The use of the oxychloride generally results in the production of selenium dioxide as a by-product. If the monochloride is used, free red selenium is precipitated often in a colloidal state. The presence of either the dioxide or free selenium introduces difficulty in purification of the desired product.

In this investigation, the action of selenium tetrachloride on various esters of salicylic acid was studied. The results obtained indicate that the first reaction taking place between selenium tetrachloride and the esters of salicylic acid gives compounds represented by formula I.

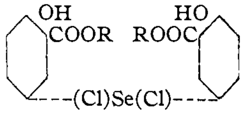
These trichloro derivatives are hydrolyzed very easily. They react slowly, as a matter of fact, with moisture from the air to yield the corresponding hydroxide (formula II).



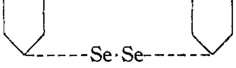
I



II



III



IV

An attempt was made to prove the presence of hydroxyl groups in compounds of formula II by acetylation with acetyl chloride. The addition of acetyl chloride, however, regenerated the trichloride (formula I) and gave acetic acid as the other product. It has been shown by Nelson[3] and co-workers that the hydroxyl group para to selenium is not acetylated.

The trichlorides of this series are yellow, hygroscopic, unstable compounds which change color slowly, and give off hydrogen chloride. The trihydroxides are grayish-white in color and seem to be stable. They are soluble in alcohol, but insoluble in ether and cold water. They react vigorously with acetyl chloride as might be expected, but yield the trichlorides.

If the selenium tetrachloride and ester are heated over a longer period of time the dichloroselenodisalicylates are formed (formula III).

The dichloroselenodisalicylates have been prepared previously by Nelson and co-workers and their properties described. They are usually yellow and quite stable. They are insoluble in ether, alcohol, and chloroform, but are soluble to

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(1) Abstract of a thesis submitted to the faculty of Purdue University by John A. Bilderback in partial fufilment of the requirements for the degree of master of science, August, 1937. Presented before the Division of Organic Chemistry of the A. C. S. at the Dallas meeting, April, 1938.

(2) Nelson and Alquist, THIS JOURNAL, **53**, 4033 (1931); Nelson and Jones, *ibid.*, **52**, 1588 (1930); Nelson, Bunting and Schroeder, *ibid.*, **55**, 801–803 (1033); Morgan and Burstall, *J. Chem. Soc.*, 3260 (1928); Godchaux, *Ber.*, **24**, 763 (1891); Nelson and Boase, *Proc. Indiana Acad. Sci* **44**. 135–137 (1934).

(3) Nelson and Baker, THIS JOURNAL, **56**, 467 (1934).

TABLE I

New compounds prepared			Color	Soluble	Insoluble	Yield, %	M. p.,[a] °C.	Selenium, % Calcd.	Selenium, % Found	Chlorine, % Calcd.	Chlorine, % Found
3-Carbo-( )-4-hydroxyphenylselenium	Trichloride	Methoxy-	Yellow	EtOH	Et_2O[b]	91	167 –168	23.52	23.60 ± 0.02	31.6	29.92 ± 0.08
		Ethoxy-	Yellow	EtOH	Et_2O[b]	82	159.1	22.52	22.5 ± .04	30.04	30.05 ± .05
		Propoxy-	Yellow	EtOH	Et_2O[b]	48	148	21.7	21.75 ± .05	29.7	28.5 ± .2
	Trihydroxide	Methoxy-	Gray-white	EtOH	Et_2O	100	162.4–162.9	28.11	28.22 ± .02		
		Ethoxy-	Gray-white	EtOH	Bz	100	142.4	26.78	26.94 ± .04		
		Propoxy-	Gray-white	EtOH	H_2O	100	115	25.56	25.57 ± .08		
Dimethyl 5,5′diselenodisalicylate			Yellow	$CHCl_3$	EtOH H_2O	30	136.1–136.6	34.35	34.36 ± .09		

[a] All compounds tend to decompose at the melting point. [b] Hydrolyzed by water.

some extent in benzene. The derivative from phenyl salicylate is grayish-white in color.

In general, if the selenium tetrachloride and ester are heated over a prolonged period, oily products result which cannot be handled satisfactorily. In certain cases cooling of the oily product gives orange-red, waxy, resinous materials.

In the case of methyl salicylate, a compound was isolated which was yellow in color, contained no chlorine, and was quite stable. It was insoluble in alcohol and water, but dissolved readily in chloroform. This compound was isolated, analyzed, and identified as indicated by formula IV, where R is CH_3.

Treatment of the other esters in a similar manner gave yellow oils which would not solidify. The probable reaction involves the dissociation of selenium tetrachloride into selenium monochloride and chlorine, followed by condensation of the selenium monochloride with the ester to give dimethyl 5,5′-diselenodisalicylate (formula IV).

In studying the reaction of phenyl salicylate, an orange-red, waxy solid was obtained by prolonged heating of the ester with selenium tetrachloride and subsequent cooling. This solid melted at 97.5–90° without decomposition. It burned with a very smoky flame. The compound analyzed as follows: selenium 6.04%; chlorine 13.98 ± 0.14%. Tentatively, this compound is assigned the formula $Se(C_6H_4(OH)COOC_6H_4Cl)_4$. Since chlorine is produced by decomposition of selenium tetrachloride, this proposed product is a possibility.

Experimental

The phenyl salicylate (salol) was obtained from the Mallinckrodt Chemical Works and used without further purification. The methyl salicylate was obtained from the Eastman Kodak Company and used without purification. The other esters were prepared by the usual ester synthesis. Part of the selenium tetrachloride used was obtained by the reaction of selenium oxychloride and acetyl chloride. The rest of the selenium tetrachloride was prepared by the chlorination of selenium suspended in anhydrous benzene free from thiophene.

Melting points were obtained by the method outlined by LaMotte.[4] All melting points listed are corrected.

The products were identified by analysis for selenium and chlorine, using the method outlined by Reid and Shaw.[5] Analysis for selenium was carried out by fusion with potassium nitrate and sodium peroxide in a Parr bomb. The fused mass was dissolved, acidified with hydrochloric acid and the selenium precipitated by means of sulfur dioxide.

Analysis for chlorine was carried out in a similar way except that nitric acid was used for acidifying, and silver chloride was precipitated by the addition of silver nitrate.

The Preparation of 3-Carbomethoxy-4-hydroxyphenylselenium Trichloride.—Twenty grams of selenium tetrachloride and 27 g. of methyl salicylate were placed in a 500-ml. three-necked round-bottomed flask equipped with an efficient wind-mill stirrer, and a reflux condenser fitted with a trap to absorb hydrogen chloride. The reaction flask is kept at room temperature. Hydrogen chloride is evolved and a brownish mass forms in the flask. This mass is then transferred to a Büchner funnel and washed thoroughly with anhydrous ether. A yellow compound is obtained which is hygroscopic and gives an odor of hydrogen chloride; m. p. 167–168°, with decomposition. The chloride analysis on this compound was low but this was to be expected as hydrogen chloride was evolved.

The other trichlorides were prepared similarly and the trihydroxides were obtained in quantitative yields by addition of water. The hydrolysis takes place immediately.

Using selenium tetrachloride, some previously prepared and described 5,5′-selenodisalicylate-Se-dichlorides were obtained in varying yields: dimethyl, 5%; diethyl, 30%; dipropyl, 17.4%; diphenyl, 5%.

Summary

1. The reaction of selenium tetrachloride on some esters of salicylic acid has been studied.

2. Numerous side reactions seem to take place which prevent obtaining good yields of the dichloroselenosalicylates with selenium tetrachloride.

3. Prolonged heating of the selenium tetra-

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[4] Nelson and LaMotte, Thesis, Purdue University, 1930, pp. 14, 15.

[5] Shaw and Reid, THIS JOURNAL, 49, 2330 (1927).

chloride and the esters produces oily or waxy residues.

4. The reaction of selenium tetrachloride on the esters of salicylic acid goes through several stages. It seems probable that a number of other compounds might be isolated if proper conditions can be found.

LAFAYETTE, INDIANA RECEIVED FEBRUARY 11, 1938

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

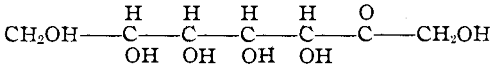
The Structure of Sedoheptulosan (Anhydro-sedoheptose)[1]

BY C. S. HUDSON

In the present article it will be shown that there is at hand, from the published work of several investigators, conclusive experimental evidence that sedoheptulosan,[2] the remarkable anhydride that is spontaneously formed from sedoheptulose in acid solution, is not related in structure to levoglucosan, as generally supposed, but contains a septanose ring and an ethylene oxide ring. This result necessitates a modification of present views regarding the stability of ring systems in carbohydrates that have the configuration which pertains in common to sedoheptulose and altrose; it may have further consequences as regards other sugars because of the new structures that it discloses.

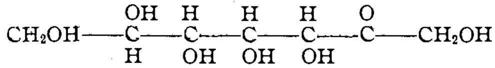
The argument requires for clearness a presentation that follows the historical order.

At the time of the discovery of sedoheptulose[2] in *Sedum spectabile*, the sugar (a ketose) was reduced by sodium amalgam to yield two heptitols which were named provisionally α- and β-sedoheptitol, and it was made probable that α-sedoheptitol is identical with volemitol, a heptitol of unknown configuration, which Bourquelot[3] had isolated from the mushroom, *Lactarius volemus;* the identity was later established by direct comparison of the two substances,[4] and by a thorough study of the derivatives of volemitol.[5] Investigation of the configuration of sedoheptulose was then undertaken by La Forge,[6] who advanced in 1920 the view that it must be either (I) or (II) or a mirror image of one of these.



$$CH_2OH-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\overset{O}{C}-CH_2OH$$

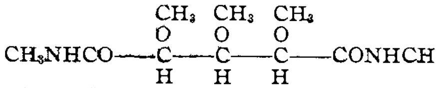
D-Alloheptulose
(I)



$$CH_2OH-\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\overset{O}{C}-CH_2OH$$

L-Taloheptulose
(II)

It is clear today that a mistake was made by La Forge in this allocation of configuration; it was corrected by Ettel in 1932 (*vide infra*) but in the meantime it had adversely affected the reasoning in a brilliant experimental investigation by Hibbert and Anderson,[7] next to be described. In 1930 these workers undertook the determination of the positions of the two rings in sedoheptulosan by methylation methods, basing the study naturally upon La Forge's configurational allocations (I) or (II). The fully methylated derivative proved to be a crystalline substance, tetramethylsedoheptulosan; its oxidation by strong nitric acid yielded a trimethoxyglutaric acid which was isolated as a crystalline dimethylamide (m. p. 145–146°, no rotation, correct analysis for C, H, N and OCH_3). Only four trimethoxyglutaric acids are possible, namely, those derivable ultimately from the four pentoses (counting the D- and L- forms of tri-methoxy-arabinoglutaric acid as two acids), and only two of these can be optically inactive, namely, the xylo- and ribo-forms; trimethoxyxylo-glutaric dimethylamide had been well studied[8] (m. p. 167–168°) and Hibbert and Anderson concluded that their substance, of much lower melting point, must be the hitherto unknown trimethoxyribo-glutaric dimethylamide (III).



$$CH_3NHCO-\underset{H}{\overset{\overset{CH_3}{O}}{C}}-\underset{H}{\overset{\overset{CH_3}{O}}{C}}-\underset{H}{\overset{\overset{CH_3}{O}}{C}}-CONHCH_3$$

Trimethoxyribo-glutaric dimethylamide
(III)

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[1] Publication authorized by the Surgeon General, United States Public Health Service.

[2] La Forge and Hudson, *J. Biol. Chem.*, **30**, 61 (1917). This name seems preferable to the original designation, *anhydro-sedoheptose*, and likewise *sedoheptulose* to *sedoheptose*.

[3] Bourquelot, *Bull. soc. mycologique de France*, **5**, 132–163 (1889). This volume is in the library of the U. S. Dept. of Agriculture, Washington, D. C.

[4] La Forge, *J. Biol. Chem.*, **42**, 375 (1920); La Forge and Hudson, *ibid.*, **79**, 1 (1928).

[5] Ettel, *Coll. Czechoslovak Chem. Comm.*, **1**, 288 (1929).

[6] La Forge, *J. Biol. Chem.*, **42**, 367 (1920).

[7] Hibbert and Anderson, *Canadian J. Research*, **3**, 306 (1930).

[8] Haworth and Jones, *J. Chem. Soc.*, 2352 (1927).