

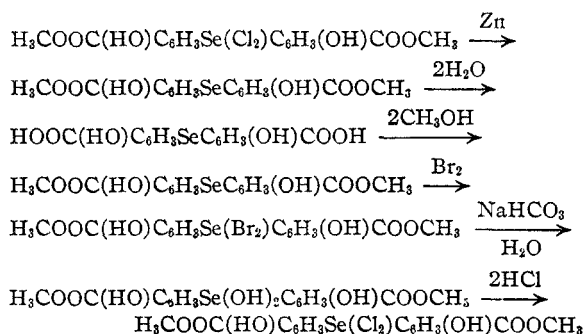
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Organic Compounds of Selenium. IV. Confirmation of the Structure of Dimethyl-5,5'-selenodisalicylate Se-dichloride

BY R. E. NELSON AND R. G. BAKER

Attempts in this Laboratory to *acylate* the phenolic group in the dialkyl 5,5'-selenodisalicylate Se-dichlorides¹ have been unsuccessful and it was considered advisable to confirm the structure of the simplest one of these compounds, namely, dimethyl-5,5'-selenodisalicylate Se-dichloride. It was thought best to change the dimethyl-5,5'-selenodisalicylate Se-dichloride by a series of conversions into 5,5'-selenodisalicylic acid prepared by Morgan and Burstall² and then convert it back into the original compound. At each stage a check was to be made by comparing the melting points with those found by previous investigators.

Plan of Conversion



The reactions above were successfully carried through, showing that the general structure of the dialkyl 5,5'-selenodisalicylate Se-dichlorides was the same as that of the 5,5'-selenodisalicylic acid prepared by Morgan and Burstall.²

The structure of 5,5'-selenodisalicylic acid has been checked by Nelson and Boase of this Laboratory³ by the following method. In an attempt to prepare 5,5'-selenodisalicylic acid Se-dibromide by the action of bromine in chloroform solution upon 5,5'-selenodisalicylic acid, the bromine instead of adding to the selenium, replaced it and the resulting product was 3,5-dibromosalicylic acid. A mixed melting point with some previously prepared 3,5-dibromosalicylic acid by the action of bromine upon salicylic acid, remained

constant at 233°. This indicates that the selenium was attached to carbon Number 5.

Experimental

The selenium oxychloride used in this work was obtained from the J. T. Baker Chemical Company and was not further purified. The methyl salicylate was obtained from the Mallinckrodt Chemical Company. The analyses were carried out by the method of Shaw and Reid.⁴

The preparation of the primary product, dimethyl-5,5'-selenodisalicylate Se-dichloride, was carried out according to the procedure given by Nelson, Schroeder and Bunting. The remainder of the reactions are well known and the results of the experimental work are given in Table I.

TABLE I

Name	Color	M. p., °C.	Yield, %	Analyses Selenium, %	
				Calcd.	Found
1 Dimethyl-5,5'-selenodisalicylate	White	158	48
2 5,5'-Selenodisalicylic acid	Light yellow	270	33	22.4	22.3
3 Dimethyl-5,5'-selenodisalicylate	Not isolated but carried directly to the next step				
4 Dimethyl-5,5'-selenodisalicylate Se-dibromide	Orange-red	146	17
5 Dimethyl-5,5'-selenodisalicylate Se-dihydroxide	White	124	11
Dimethyl-5,5'-selenodisalicylate Se-dichloride	Light yellow	171

The final product was checked by taking a mixed melting point of it with some of the original compound before it was converted. The melting point remained the same. The yield in each case was based on the primary product and the yield of the final product was naturally small.

Summary

1. Morgan and Burstall's theory of the position of the selenium in 5,5'-selenodisalicylate has been confirmed by a distinct set of reactions.

2. The structure of the dialkyl 5,5'-selenodisalicylate Se-dichlorides and related compounds has been established.

LAFAYETTE, IND.

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(1) Nelson, Schroeder and Bunting, *THIS JOURNAL*, **55**, 801 (1933).

(2) Morgan and Burstall, *J. Chem. Soc.*, 3260 (1928).

(3) Nelson and Boase, unpublished work.

(4) Shaw and Reid, *THIS JOURNAL*, **49**, 2330 (1927).