sodium sulfate and fractionated to give 24.9 g. (97%) of tetra-*n*-butylsilane: b. p. 156–157° (22 mm.); d^{20}_4 0.8008 and d^{22}_4 0.8002; $n^{20}\mathrm{D}$ 1.4465 and $n^{22}\mathrm{D}$ 1.4460; *MR*D 85.47 (calcd. *MR*D 85.49).

Anal.[11] Calcd. for $C_{16}H_{36}Si$: Si, 10.93. Found: Si, 11.12.

From a similar preparation using 20.8 g. (0.1 mole) of ethyl silicate and 0.41 mole of *n*-butyllithium there was obtained 22.4 g. (95%) of tetra-*n*-butylsilane: b. p. 156–157° (22 mm.); d^{20}_4 0.8010; $n^{20}\mathrm{D}$ 1.4463.

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[11] It should be mentioned here that the method of analysis now being used by us for relatively non-volatile organosilicon compounds involves oxidation by means of conc. sulfuric acid, the platinum crucible being heated in a Rogers ring burner. This procedure is better than the one described recently [Gilman, Clark, Wiley and Diehl, THIS JOURNAL, **68**, 2728 (1946)] in which perchloric acid is used.

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Preparation of a Series of *p*-Toluenesulfilimines[1]

BY THOMAS P. DAWSON[2]

The condensation of chlorosulfides with sodium toluene-*p*-sulfonchloroamide to form compounds containing quadrivalent sulfur was first discovered by Raper,[3] and later investigated by Mann and Pope.[4] Recently, Fuson,[5] *et al.*, have reported the *p*-toluenesulfilimine of several additional chlorosulfides.

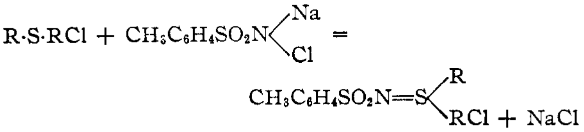
TABLE I

ANALYSES AND PROPERTIES OF SUBSTITUTED SULFINE-*p*-TOLUENE SULFILIMINES

Substituent	Form	M. p., °C.	Formula	Chlorine Calcd. %	Chlorine Found %	Sulfur Calcd. %	Sulfur Found %
2-Chloroethyl *n*-propyl	Needles	118–119	$C_{12}H_{18}O_2ClNS_2$	11.52	11.37	20.83	20.72
2-Chloroethyl *n*-butyl	Rect. or sq. plates	117–118	$C_{13}H_{20}O_2ClNS_2$	11.02	10.77	19.92	19.59
2-Chloroethyl *i*-amyl	Tri. or hex. rods	91–92	$C_{14}H_{22}O_2ClNS_2$	10.56	10.85	19.08	18.82
2-Chloroethyl benzyl	Rect. pl. in clusters	133–134	$C_{16}H_{18}O_2ClNS_2$	9.97	10.18	18.02	18.36
2-Chloropropyl ethyl[a]	Square plates	119–120	$C_{12}H_{18}O_2ClNS_2$	11.52	11.52	20.83	19.42
3-Chloropropyl ethyl	Plates	86–87	$C_{12}H_{18}O_2ClNS_2$	11.52	11.59	20.83	20.77
bis-(2-Chloropropyl)	Cl. of short rods	169–170	$C_{13}H_{19}O_2Cl_2NS_2$	19.90	20.00	18.00	17.90
bis-(Chloromethyl)[b]	Needles	101–102	$C_9H_{11}O_2Cl_2NS_2$	...	...	...	...
2-Bromoethyl ethyl	Rectangular	146	$C_{11}H_{16}O_2BrNS_2$	23.63	23.43	18.96	19.06

[a] Fuson, *et al.*, *J. Org. Chem.*, **11**, 469 (1946). [b] Prepared by Mann and Pope[4] and confirmed by us.

In connection with certain chemical warfare projects in 1928 this type of reaction was studied and eight new compounds of the sulfilimine type were isolated. The following equation represents the mechanism of the reaction.



$$\mathrm{R{\cdot}S{\cdot}RCl} + \mathrm{CH_3C_6H_4SO_2N}\!\!\begin{array}{l}\diagup \mathrm{Na}\\ \diagdown \mathrm{Cl}\end{array} = \mathrm{CH_3C_6H_4SO_2N{=}S}\!\!\begin{array}{l}\diagup \mathrm{R}\\ \diagdown \mathrm{RCl}\end{array} + \mathrm{NaCl}$$

Procedure.—All of the sulfilimines were prepared by the same general procedure as follows: An aqueous solution of 0.04–0.10 mole of sodium toluene-*p*-sulfonchloroamide (chloramine-T) was prepared in 100 cc. of water and 0.04–0.10 mole of the sulfide, which had previously been dissolved in 75 to 100 cc. of acetone, was added dropwise with continuous stirring. In some cases the reaction was complete in thirty minutes while in others several days were required for a complete condensation. When the reaction was complete the product, which sometimes came down as an oil, was washed several times with water to dissolve any excess of chloramine-T and finally with ether which removed any unreacted sulfide. It was then crystallized several times from an appropriate solvent until a constant melting point was obtained. The compounds prepared were all white crystalline solids of definite melting point. They are recorded in the following table together with some of their physical and chemical properties.

The author is grateful to Dr. Walter E. Lawson who offered assistance during the course of this work.

The experimental work reported in this paper was completed in November, 1938.

EDGEWOOD ARSENAL, MD. RECEIVED DECEMBER 23, 1946

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[1] Published with the permission of the Chief, Chemical Corps.

[2] Chemical Corps Technical Command, Edgewood Arsenal, Md.

[3] Report to the British Chemical Warfare Service.

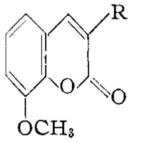
[4] Mann and Pope, *J. Chem. Soc.*, **121**, 1052 (1922); *ibid.*, **123**, 1172 (1923).

[5] Fuson, *et al.*, *J. Org. Chem.*, **11**, 469 (1946).

Coumarins from 2-Hydroxy-3-methoxybenzaldehyde

BY E. C. HORNING AND M. G. HORNING

In studying condensations of derivatives of 2,3-dihydroxybenzaldehyde with active methylene compounds, we have had occasion to prepare a number of coumarins from 2-hydroxy-3-methoxybenzaldehyde and esters, $RCH_2COOC_2H_5$. The condensation was carried out by the Knoevenagel[1] method, using piperidine as a catalyst. The reactions proceeded readily, but the yields of coumarins varied considerably with different esters. The following 8-methoxycoumarins were prepared.



I R = —COC_6H_5
II R = —$COCH_3$
III R = —CN
IV R = —$COOC_2H_5$
V R = —$COCH_2COOC_2H_5$

Experimental

To a solution of 1.50 g. (0.01 mole) of 2-hydroxy-3-methoxybenzaldehyde in 20 ml. of warm absolute ethanol was added 0.011 mole of the ester and 3 drops of piperidine. The solution was heated under reflux for five minutes. After chilling, the crystalline product was removed by filtration and washed with absolute alcohol.

The yields, melting points and analytical data are given in Table I.

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[1] Knoevenagel, *Ber.*, **31**, 2585 (1898).