

after five minutes, indicate that Criegee's method can be used for the quantitative determination of compounds that are soluble only in water. The advantages of this method are obvious: whereas the periodate oxidation requires many hours—forty-eight hours in the case of adenylic acid derivatives¹—the oxidation with lead tetraacetate is complete within a few minutes.

Wormith and Rae⁸ succeeded in titrating α -glycerophosphate in the presence of the β -isomer by means of lead tetraacetate in aqueous medium. These authors, however, allowed a period of six hours for the completion of the oxidation. In order to increase the solubility of the calcium and barium salts of these esters they had to add hydrochloric acid which they state decreases the oxidizing power of lead tetraacetate. The question arises as to whether the time of oxidation could not be appreciably shortened by the use of the soluble sodium salts.

(8) Wormith and Rae, *THIS JOURNAL*, **63**, 2523 (1941).

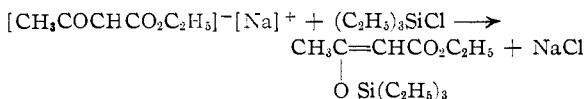
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Ethyl β -Triethylsiloxycrotonate and Tetra-*n*-butylsilane

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In connection with the preparation of some cyclic organosilicon compounds an examination was made of the reaction between sodioacetoacetic ester and triethylsilyl chloride to determine whether ethyl α -triethylsilylacetate might be formed. However, the only product isolated was ethyl β -triethylsiloxycrotonate.



Hydrolysis of the siloxycrotonate by 10% hydrochloric acid gave acetone and hexaethylidisiloxane. Reaction of the siloxycrotonate with acetyl chloride yielded triethylsilyl chloride and ethyl β -acetoxyacrylate. It is possible that the procedure described by Hauser and co-workers¹ for C-alkylation with *t*-butyl alcohol by means of boron trifluoride might give some of the compound from triethylsilanol and acetoacetic ester.

In a study of group and bond refractions in organosilicon liquids, Sauer² has raised a question on a supposed tetra-*n*-butylsilane prepared³ from ethyl silicate and *n*-butylmagnesium bromide. The molar refraction of that product is at variance with the value calculated for tetra-*n*-butylsilane and in agreement with that for tri-*n*-butyl-

(1) Adams, Abramovitch and Hauser, *THIS JOURNAL*, **65**, 552 (1943).

(2) Sauer, *ibid.*, **68**, 954 (1946).

(3) Post and Hofrichter, *J. Org. Chem.*, **5**, 572 (1940); see, also, Tseng and Chao, *Science Repts. Natl. Univ. Peking*, **1** (No. 4), 21 (1936) [*C. A.*, **31**, 655 (1937)].

ethoxysilane. We have prepared tetra-*n*-butylsilane in excellent yields by reaction of *n*-butyllithium with ethyl silicate and with silicon tetrachloride. The compound prepared by these reactions⁴ has a molar refraction in agreement with that for the R_4Si compound, and physical constants unlike those reported for the product from ethyl silicate and *n*-butylmagnesium bromide.

Experimental

Ethyl β -Triethylsiloxycrotonate.—Sodioacetoacetic ester was prepared⁵ by adding 6.5 g. (0.05 mole) of ethyl acetoacetate in 30 cc. of dry toluene to 1.12 g. (0.05 g. atom) of sodium sand and 100 cc. of toluene. To the clear, stirred resulting solution was added 7.5 g. (0.05 mole) of triethylsilyl chloride⁶ in 30 cc. of dry toluene, and the resulting mixture was heated between 80–100° for twelve hours. The mixture was filtered, the filtrate distilled free of solvent, and the residue fractionated to give 7.4 g. (61%) of compound distilling at 108–110° (6 mm.), n_D^{20} 1.4560, d_4^{20} 0.9590, M_{RD} 69.42 (calcd. M_{RD} , 69.12).

Anal. Calcd. for $\text{C}_{12}\text{H}_{24}\text{O}_4\text{Si}$: Si, 11.48. Found: Si, 11.54.

Reaction with 2,4-dinitrophenylhydrazine gave only the 2,4-dinitrophenylhydrazone of ethyl acetoacetate⁷ (mixed m. p.).

A mixture of 2.44 g. (0.01 mole) of the siloxycrotonate in 50 cc. of 10% hydrochloric acid was refluxed for one-half hour. The cooled organic layer was separated, taken up in ether, dried, and fractionated to give hexaethylidisiloxane; M_{RD} 75.88 (calcd. M_{RD} 76.07). The aqueous layer was treated with benzaldehyde, and the product isolated was dibenzalacetone⁸ (mixed m. p.).

A solution of 4.9 g. (0.02 mole) of the siloxycrotonate and 1.58 g. (0.02 mole) of freshly distilled acetyl chloride was heated for six hours at 135–150°. Fractional distillation of the product gave two compounds, one of which was triethylsilyl chloride.

Anal. Calcd. for $\text{C}_6\text{H}_{15}\text{ClSi}$: Si, 18.62. Found: Si, 18.85.

The other compound distilled at 206–209° (736 mm.); n_D^{15} 1.4466; d_4^{15} 1.0664. One-half of this product was refluxed for one hour with 10% hydrochloric acid, and the hydrolysate gave no test for acetylacetone. The other half was made basic with a sodium hydroxide solution and then treated with benzaldehyde to give dibenzalacetone. Acetone is an expected hydrolysis product of ethyl β -acetoxyacrylate.

Tetra-*n*-butylsilane.—To 17 g. (0.1 mole) of silicon tetrachloride in 100 cc. of ether was slowly added, in a nitrogen atmosphere, 0.41 mole of *n*-butyllithium⁹ in 350 cc. of ether. The reaction flask was immersed in an ice-bath, and the rate of addition was such as to maintain a gentle reflux. Finally, the mixture was refluxed for one-half hour. Subsequent to hydrolysis of the cooled mixture, the ether layer was separated, and washed with concd. sulfuric acid to remove any silanol.¹⁰ The ether layer was separated, washed with water, dried over

(4) Gilman and Clark, *THIS JOURNAL*, **68**, 1675 (1946). We inadvertently omitted mention in this article of a patent which was reported in *C. A.* of this year by Fleming, U. S. Patent 2,386,452 [*C. A.*, **40**, 603 (1946)] on the preparation of some unsymmetrical silicon compounds by means of RLi compounds.

(5) Breslow, Yost, Walker and Hauser, *ibid.*, **66**, 1921 (1944).

(6) DiGiorgio, Strong, Sommer and Whitmore, *ibid.*, **68**, 1380 (1946).

(7) Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 255.

(8) Huntress and Mulliken, *ibid.*, p. 374.

(9) Gilman, Zoellner and Selby, *THIS JOURNAL*, **55**, 1252 (1933); Gilman and Stuckwisch, *ibid.*, **65**, 1461 (1943); Gilman and Haubein, *ibid.*, **66**, 1515 (1944). This last reference describes the analytical procedure used.

(10) Friedel and Crafts, *Ann. chim. phys.*, **4**, 19 (1895).

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}_D 1.4465 and n^{22}_D 1.4460; M_R 85.47 (calcd. M_R 85.49).

Anal.¹¹ Calcd. for $C_{18}H_{38}Si$: 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}_D 1.4463.

(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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(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.

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Preparation of a Series of *p*-Toluenesulfilimines¹

By THOMAS P. DAWSON²

The condensation of chlorosulfides with sodium toluene-*p*-sulfonylchloroamide 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.

Coumarins from 2-Hydroxy-3-methoxybenzaldehyde

By E. C. HORNING AND M. G. HORNING

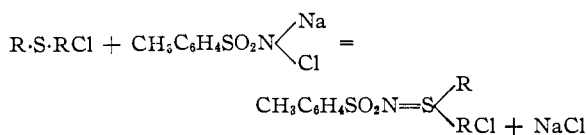
In studying condensations of derivatives of 2,3-dihydroxybenzaldehyde with active methylene compounds, we have had occasion to prepare a number of coumarins from 2-hydroxy-3-methoxybenzaldehyde and esters, $RCH_2COOC_2H_5$. The condensation was carried out by the Knoevenagel¹

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

Substituent	Form	M. p., °C.	Formula	Chlorine		Sulfur	
				Calcd. %	Found %	Calcd. %	Found %
2-Chloroethyl <i>n</i> -propyl	Needles	118–119	$C_{12}H_{18}O_2ClNS_2$	11.52	11.37	20.83	20.72
2-Chloroethyl <i>n</i> -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>i</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	$C_{15}H_{18}O_2ClNS_2$	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

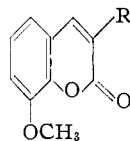
^a Fuson, *et al.*, *J. Org. Chem.*, **11**, 469 (1946). ^b Prepared by Mann and Pope⁴ and confirmed by us.

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.



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*-sulfonylchloroamide

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 = $-COOC_2H_5$
 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.

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

(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).