(26.5 g., 0.14 mole) in 40 ml. of dry ether with 50 mg. of PtO_2 was hydrogenated to give the paraffin (25.5 g., 0.132 mole, 94% including estimates in fore and tail cuts) boiling 97.5–99.5°. The olefin free spectra was superimposable with that obtained by Carr on a sample prepared by another method and having the constants: b.p. 99°, n_D^{20} 1.3103, and d_4^{20} 1.231. (My data for a purified sample: b.p. 99°, n_D^{20} 1.3105, and d_4^{20} 1.232.)

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COLUMBUS, OHIO

[CONTRIBUTION FROM THE ROHM & HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION]

Preparation of Esters of Pentaerythritol Arsenite and of Other Pentaerythritol Esters

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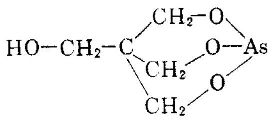
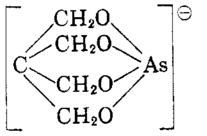
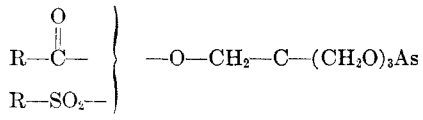
Several esters of pentaerythritol arsenite (I) have been prepared. The arsenite ester portion of these compounds was found to be selectively hydrolyzed, acetolyzed, or nitrolyzed to produce the corresponding pentaerythritol monoester, the pentaerythritol ester triacetate, or the ester of pentaerythritol trinitrate.

Esters of pentaerythritol can be prepared in several ways,[1] but selective partial esterification is not easily carried out. One obvious method of preparation of pentaerythritol monoesters would be that of blocking three of the hydroxyl groups with some functional group that could be removed readily. Such a monofunctional pentaerythritol, the product obtained by merely heating a mixture of arsenic trioxide and pentaerythritol and removing the water formed, is pentaerythritol arsenite, I.[2] This compound, m.p. 106–107°, also has been formulated as II and designated pentaerythritol arsenious acid.[3] However, the infrared spectrum of pentaerythritol arsenite which possessed the characteristic hydroxyl absorption at 3420 cm.$^{-1}$ (Nujol mull), and the facile esterification of the arsenite support the structure (I) originally formulated by Englund.


I


II

Esterification of I by the conventional methods outlined in the experimental section to produce the carboxylic or sulfonic acid esters III proceeded readily. The esters prepared are listed in Table I.



$$\left.\begin{array}{l} R-\overset{O}{\overset{\|}{C}}- \\ R-SO_2- \end{array}\right\} -O-CH_2-C-(CH_2O)_3As$$

III

These esters and the arsenite I were not hygroscopic, but were hydrolyzed on contact with water. Because these esters were susceptible to hydrolysis, isolation was accomplished by evaporating the reaction mixture to dryness and then either extracting the ester into petroleum ether (Method B, Table I) or by adding cold methanol to remove the pyridine hydrochloride and leave the ester as a residue (Method C, Table I). Pentaerythritol acetate arsenite, however, was prepared from isopropenyl acetate and pentaerythritol arsenite (Method A, Table I), and the acetate was distilled directly from the reaction mixture.

As expected, the pentaerythritol arsenite esters hydrolyzed to produce the corresponding pentaerythritol monoesters. This hydrolysis was carried out efficiently by placing a methylene chloride solution of the arsenite ester on a short silica gel column and eluting the hydrolyzed product with methanol in methylene chloride. The pentaerythritol monoesters prepared in this way are listed in Table II.

Acetolysis of some of the arsenite esters III was carried out to produce the corresponding ester triacetate. This reaction proceeded readily on mixing the ester III, acetic anhydride, and a catalytic amount of sulfuric acid. In addition to pentaerythritol tetracetate, pentaerythritol tosylate triacetate, m.p. 70° and pentaerythritol benzoate triacetate, m.p. 95°, were prepared in this manner.

The nitrolysis of the arsenite esters to produce an organic acid ester of pentaerythritol trinitrate[4] also appeared to be a general reaction. Both pentaerythritol arsenite *p*-toluenesulfonate and pentaerythritol arsenite acetate were converted to the trinitrate esters on treatment with 90% nitric acid at 0°. The same nitration procedure

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(1) E. Berlow, R. H. Barth, and J. F. Snow, *The Pentaerythritols*, Reinhold Publishing Corporation, New York, N.Y., 1958, pp. 212–58.

(2) B. Englund, *J. prakt. Chem.*, **124**, 191 (1930).

(3) Ref. (1) p. 50.

(4) N. S. Marans, D. E. Elrick, and R. F. Preckel, *J. Am. Chem. Soc.*, **76**, 1304 (1954).

TABLE I

Preparation of Pentaerythritol Arsenite Esters

Arsenite Ester	M.P., °C.	Yield, %	Method of Preparation[a]	Anal. Calcd. C	Anal. Calcd. H	Anal. Calcd. As	Anal. Found C	Anal. Found H	Anal. Found As
Acetate	90–91.5	88	A	33.62	4.43	29.96	33.71	4.54	30.13
Propionate	55–57	48	B	36.68	4.96	28.36	36.05	5.07	28.95
Caproate	40–42	49	B	43.15	6.26	24.47	43.12	6.38	24.63
Benzoate	133–134	60	C	46.17	4.20	24.00	45.82	4.29	24.54
Benzenesulfonate	138–139	37	C	37.94	3.76	21.51	38.22	4.22	22.15
p-Toluenesulfonate	177–178	73	C	39.71	4.26	20.77	39.79	4.17	20.68
m-Nitrobenzoate	159–161	64	C	40.55	3.39	. . .	40.14	3.47	. . .

[a] Methods outlined in experimental section.

TABLE II

Pentaerythritol Monoesters

Ester	M.P., °C.	Analysis Calcd. C	Analysis Calcd. H	Analysis Found C	Analysis Found H
Acetate	69–70[4]	. . .	. . .	. . .	. . .
Propionate	15–17	49.99	8.39	49.22	8.64
Caproate	20–22	56.39	9.47	56.27	9.98
Benzoate	86–87	59.44	6.71	59.27	6.84
p-Toluenesulfonate	73–74	49.64	6.25	49.15	6.15
Benzenesulfonate	60–62	47.81	5.84	48.11	6.06
m-Nitrobenzoate	120–121	50.52	5.30	50.10	5.59
p-Nitrobenzoate[a]	141–142	50.52	5.30	50.61	5.16

[a] Arsenite ester was not purified.

has been used to convert pentaerythritol monoacetate to the trinitrate.[4]

EXPERIMENTAL[5]

Reaction of pentaerythritol and arsenic trioxide. The procedure outlined by Englund[2] was followed using 54.4 g. (0.40 mole) of pentaerythritol and 39.6 g. (0.20 mole) of arsenic trioxide. The mixture began to melt at 80° and water began to distill from the flask when the reaction temperature reached 120°. The mixture was quickly heated to 230° and then allowed to cool. Distillation of the residue gave pentaerythritol arsenite (I), 77 g. (93%), b.p. 140° (1 mm.), m.p. 106–107°, reported 102–103°.[2]

Preparation of pentaerythritol arsenite esters. Method A. Preparation of pentaerythritol arsenite acetate. A mixture of pentaerythritol (27.2 g., 0.20 mole) and arsenic trioxide (19.8 g., 0.10 mole) was heated to 230° as described above. The mixture was allowed to cool to 60°, and isopropenyl acetate (24 ml., 0.22 mole) then was added with stirring. Addition of 0.5 g. of *p*-toluenesulfonic acid monohydrate resulted in an exothermic reaction which was controlled by external cooling. When the exotherm had subsided the reaction mixture was heated at 100° for 1 hr. and acetone was allowed to distill from the reaction mixture. The mixture was warmed to 130°, 0.10 g. of magnesium carbonate was added, and the contents of the flask were distilled. There was thus obtained pentaerythritol arsenite acetate, 44 g. (88%), b.p. 125–127° (1 mm.). The acetate slowly solidified and melted at 90–91.5° after recrystallization from ligroin.

Method B. Preparation of pentaerythritol arsenite propionate. A solution of 10.4 g. (0.05 mole) of pentaerythritol arsenite in 20 ml. of pyridine was cooled to keep the temperature of the reaction mixture below 30° while 4.5 ml. (0.51 mole) of propionyl chloride was added over a 5-min. period. The reaction mixture was stirred at 45–50° for 2 hr., then excess pyridine and propionyl chloride were removed at reduced pressure. To the solid residue was added 150 ml. of ligroin and the mixture was refluxed for 15 min. The ligroin was decanted and chilled in dry ice, and was then filtered to remove a semisolid. Flash distillation of the semisolid at 130° (0.5 mm.) gave pentaerythritol arsenite propionate, 6.3 g., (48%), m.p. 55–57°.

Method C. Preparation of pentaerythritol arsenite p-toluenesulfonate. To a stirred solution of 10.4 g. of pentaerythritol arsenite in 20 ml. of pyridine 9.5 g. of *p*-toluenesulfonyl chloride was added portionwise. The reaction mixture slowly exothermed to 42°; when the exotherm subsided the mixture was maintained at 45–50° for 2 hr. The excess pyridine was then removed at reduced pressure. The residue was triturated with 50 ml. of absolute methanol at 0°, and was then filtered to give pentaerythritol arsenite *p*-toluenesulfonate, 13.2 g., m.p. 170–173°. Recrystallization from methanol raised the m.p. to 177–178°.

Hydrolysis of pentaerythritol arsenite esters. The method used to convert the arsenite esters of Table I to the pentaerythritol monoesters listed in Table II is illustrated by the procedure given below for the hydrolysis of pentaerythritol arsenite *p*-toluenesulfonate.

A 1.0 g. sample of pentaerythritol arsenite *p*-toluenesulfonate dissolved in methylene chloride was placed on a 1-in. by 6-in. column of silica gel packed in methylene chloride. The column was eluted with 200 ml. methylene chloride, 300 ml. of methylene chloride–ethyl acetate (9:1) and 500 ml. of methylene chloride–methanol (6:1). The solid eluted by the last eluent was recrystallized from ethyl acetate–ligroin to give of pentaerythritol monotoluenesulfonate, 0.63 g., (75%), m.p. 73–74°.

Preparation of pentaerythritol p-toluenesulfonate triacetate. To a suspension of 2.0 g. of pentaerythritol arsenite *p*-toluenesulfonate in 15 ml. of acetic anhydride was added 2 drops of concentrated sulfuric acid. A slightly exothermic reaction occurred and within 1 hr. all material had dissolved. The mixture was allowed to stand at ambient temperature for 24 hr., and then was poured into 150 ml. of water. After 1 hr. the water was decanted from an oily residue. This residue was dried and then recrystallized from ligroin to give pentaerythritol triacetate tosylate, m.p. 70–71°.

Anal. Calcd. for $C_{18}H_{24}SO_9$: C, 51.91; H, 5.81. Found: C, 51.92; H, 5.93.

Preparation of pentaerythritol benzoate triacetate. The procedure outlined above was used for the preparation of pentaerythritol benzoate triacetate, m.p. 95–96°.

Anal. Calcd. for $C_{18}H_{22}O_8$: C, 59.00; H, 6.05. Found: C, 59.30; H, 6.29.

Preparation of pentaerythritol acetate trinitrate. An air-sparged solution of 0.4 g. of urea dissolved in 40 ml. of 90% nitric acid was stirred at 0° while 4.7 g. of pentaerythritol arsenite acetate was added over 5 min. There was a slight exotherm during the addition process. The mixture was stirred at 0° for an hour and at 5–10° for an additional hour. Methylene chloride (75 ml.) was added and the reaction

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(5) All melting points and boiling points are uncorrected.

mixture poured on ice. The mixture was filtered to remove arsenic trioxide and the organic layer was separated and washed with water and dilute sodium bicarbonate solution. Evaporation of the methylene chloride left pentaerythritol acetate trinitrate, 5.7 g. (97%), m.p. 86–87°. One recrystallization from ethanol gave 5.0 g. of product, m.p. 87–88°, reported 87–88°.[4]

Preparation of pentaerythritol p-toluenesulfonate trinitrate. The procedure outlined for the nitration of pentaerythritol arsenite acetate was followed using 0.3 g. of urea, 30 ml. of nitric acid, and 3.0 g. of pentaerythritol *p*-toluenesulfonate arsenite. Two recrystallizations of the product from methanol gave pentaerythritol *p*-toluenesulfonate trinitrate, 2.97 g., m.p. 96–98°, reported 97–100°.[4]

HUNTSVILLE, ALA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, SCIENTIFIC LABORATORY OF THE FORD MOTOR COMPANY]

Preparation, Properties, and Infrared Spectra of 2,6-Disubstituted Phenoxysilanes

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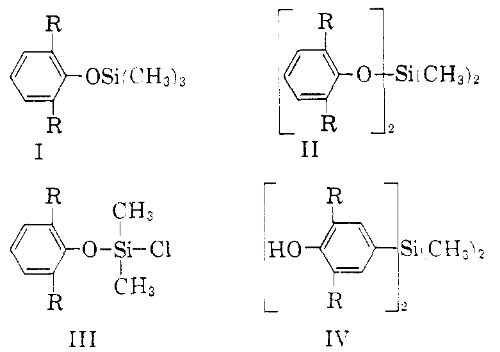
Two series of 2,6-disubstituted-phenoxy di- and trimethylsilanes in which the 2,6-substituents are H—, CH_3—, and $(CH_3)_2$-CH— groups are reported. Attention is called to the intense absorption band in the 10–11 μ region of the infrared absorption spectra of these compounds that appears to be characteristic of the Si-O-phenyl linkage.

In conjunction with studies on improving the thermal and hydrolytic stability of some organosilicon compounds, two series (I and II) of 2,6-disubstituted-phenoxy silanes were prepared. An additional chloro-derivative, IIIc, was also prepared as an intermediate for conversion to a disiloxane derivative. Only two of the compounds reported here, Ia[1] and IIa[2,3] have been reported in the literature.



I II III IV

a. R = H—
b. R = CH_3—
c. R = $(CH_3)_2CH$—

The phenoxy silanes were prepared by first converting the respective phenol to its bromomagnesium salt (reacting the phenol with methylmagnesium bromide in tetrahydrofuran) followed by treating this intermediate with dimethyldichlorosilane or trimethylchlorosilane. For laboratory-scale preparations this procedure was found more expedient than the conventional methods of preparing the alkali metal phenoxides, especially in the case of the more hindered phenols.

Di-*tert*-butylphenol, when subjected to this sequence of reactions, failed to yield a silicon derivative and the starting materials were recovered. Due to steric factors it was initially anticipated that the product would have structure IV rather than II in accord with the work of Coffield, Filbey, Ecke, and Kolka[4] on 2,6-disubstituted phenoxides. Very recently, however, Kornblum and Lurie[5] have shown that a new factor, homogeneity *vs.* heterogeneity, is of paramount importance in this type reaction. Oxygen alkylation is obtained in homogeneous solutions and the truly heterogeneous reaction gives exclusively carbon alkylation. This factor correlates well with Coffield's[4] work and also the findings reported here. Our reaction mixtures were homogeneous and we obtained only oxygen alkylation.

Several attempts were made to hydrolyze IIIc to the corresponding silanol for subsequent conversion to the disiloxane; however, hydrolytic cleavage of the 2,6-diisopropylphenoxy group occurred simultaneously.

The physical properties of the various derivatives reported here are summarized in Table I.

Infrared absorption spectra. The infrared spectra of the derivatives reported here were recorded on a Perkin-Elmer Infracord, Model 137 in the 2.5–15.0 μ region. All spectra were taken from capillary films between sodium chloride windows with the exception of bis(2,6-diisopropylphenoxy)dimethylsilane (IIc), which was prepared as a Nujol mull. The spectra are reproduced in Figs. 1 and 2.

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(1) S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

(2) P. D. George and A. E. Newkirk, U. S. Patent 2,837,552 (1958).

(3) E. Larsson, *Chem. Ber.*, **86**, 1382 (1953).

(4) T. H. Coffield, A. H. Filbey, G. G. Ecke, and A. J. Kolka, *J. Am. Chem. Soc.*, **79**, 5019 (1957).

(5) K. Kornblum and A. P. Lurie, *J. Am. Chem. Soc.*, **81**, 2705 (1959).