TABLE I

PROPERTIES OF NEW COMPOUNDS

Compound	B.p., °C.	d^{20}_4	Mol. wt. (Dumas) Found	Mol. wt. (Dumas) Calcd.	I, % Found		I, % Calcd.	Distillation range °C. uncor.	Distillation range Mm.
Me_2SiI_2	170 ± 1	2.203	306	312	81.5	81.8	81.3	168.0–168.5	760
$MeSiI_3$	229 ± 1	2.946	401	424	89.4	90.4	89.8	123.5–124.5	69
SiI_4	290[6]	...	...		..	..		....	
n-$PrSiI_3$	268 ± 2	2.552	461	452	84.6	83.6	84.3	142–143	20
i-$PrSiI_3$	267 ± 2	2.563	436	452	83.3	84.1	84.3	135–136	12
n-$BuSiI_3$	284 ± 2	2.400	450	466	81.2		81.5	151–152	12
n-$AmSiI_3$	299.5 ± 2	2.311	495	480	79.5		79.5	151–152	12

propyltriiodosilane, accompanied by 4 g. of a tarry by-product probably produced by hydrolysis.

Dimethyldiiodosilane.—Application of the standard process to 130 g. of purified dimethyldichlorosilane yielded 150 g. of dimethyldiiodosilane. Unless precautions are taken to exclude water this product may be contaminated by cyclic dimethylsiloxanes[3] which boil from 133° upward.

Other Alkyliodosilanes.—For each mole of chlorine in the alkylchlorosilane 2.30 moles of aniline was used; in the first stage the excess of aniline need not be great, but it is advisable to check its presence after filtration; in the reaction with hydrogen iodide it is advisable to filter the supposedly complete precipitate and then pass hydrogen iodide in again for a few minutes. Throughout this work equipment with ground joints was used. All six compounds were distilled in the presence of copper powder and stored in sealed tubes with a small amount of copper powder; yields averaged 60%.

Chemical Properties.—There is much variation in the vigor and in the rate of hydrolysis. In each case the compound was shaken with an equal volume of water at 25°, with the following results: methyltriiodosilane reacts vigorously, with spattering; dimethyldiiodosilane reacts vigorously, but without spattering; *n*-propyltriiodosilane reacts slowly at first, although vigorously after two minutes; *n*-butyltriiodosilane reacts vigorously after two minutes; *n*-amyltriiodosilane does not hydrolyze as easily as the others, and a self-filling micropipet[4] could be used in the analysis; *i*-propyltriiodosilane reacts quite mildly, with a temperature rise of approximately 10° only. Steric effects may be responsible for the differences between the *n*-propyl and the isopropyl derivatives. All six alkyliodosilanes react rapidly with ethanol, without any precipitation. The vapors of these compounds are somewhat inflammable at temperatures above the boiling points.

Physical Properties.—All six alkyliodosilanes are colorless mobile liquids. However, they tend to foam during the measurement of the boiling point, which could therefore be determined to one degree only. Because of the ease of hydrolysis, the determination of density was difficult in the usual pycnometer,[4] notably so with the monomethyl derivative. Only triiodofluorosilane and diiododifluorosilane[5] are more difficult to handle.

Analyses.—The method of analysis previously used[2] consisting of solution in excess ethanolic sodium hydroxide solution and back-titration with acid was suitable. All molecular weights were determined by the Dumas method.[6]

Further Study of the Ruff Method.—To establish some of the limitations of the Ruff aniline method,[1] a number of small-scale tests were carried out in benzene solution. Aniline reacts rapidly with $SiCl_4$, $SiBr_4$, $MeSiBr_3$ and $MeSiI_3$, fairly rapidly with $Si(NCO)_4$, *n*-$BuSi(NCO)_3$ and *n*-$PrSi(NCS)_3$, the criterion being 40% completion within an hour; aniline and $(C_6H_5)_2Si(NCO)_2$ gave considerable reaction after 15 hours; Et_3SiCl did not react[2] in a clean-cut fashion; aniline and $Et_2Si(NCS)_2$, or $Et_3Si(NCS)$ or $(EtO)_4Si$ did did not react at all.

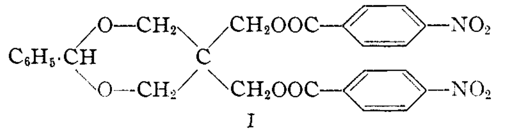
CARLINVILLE, ILLINOIS RECEIVED JUNE 15, 1950

An Unusual Orthoester of Pentaerythritol

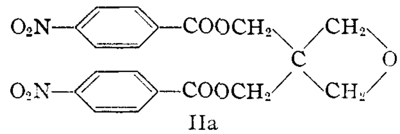
BY ERNST D. BERGMANN, ELIAHU BOGRACHOV AND S. PINCHAS

When benzylidenepentaerythritol di-*p*-nitrobenzoate (I) is treated with 4-nitrophenylhydrazine or 2,4-dinitrophenylhydrazine and hydrochloric acid in glacial acetic acid, the nitrated phenylhydrazone of benzaldehyde separates and a second crystalline compound is formed, which has not the expected composition of pentaerythritol di-(*p*-nitrobenzoate),[1] but contains one mole of water less.

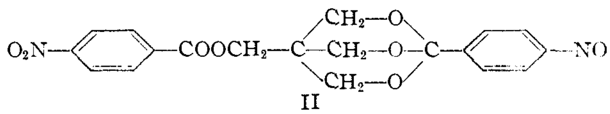
Infrared analysis revealed the absence of free hydroxyl groups, boiling formic acid, acetyl chloride and acetic anhydride caused no reaction, and also the Zerewitinoff analysis gave a negative result. The formula (IIa) of a substituted trimethylene oxide is incompatible with the negative response to acetyl chloride, as Derick and Bissell[1a] have shown trimethylene oxide to yield γ-chloropropyl acetate with this reagent. The infrared spectrum led to the conclusion that the product was an ortho-ester (II); the spectrum is not in accord with (IIa).



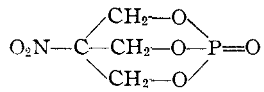
I



IIa



II



III

The spectrum (Fig. 1) shows four absorption bands, at 1178, 1118, 1103 and 1048 cm.$^{-1}$, characteristic of the C–O–C–O–C grouping, *e. g.*, in acetals.[2] In intensity, the third band exceeds even the very high absorption coefficient of the third

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[3] M. J. Hunter, J. F. Hyde, E. L. Warrick and H. J. Fletcher, THIS JOURNAL **68**, 667 (1946).

[4] H. H. Anderson, *Anal. Chem.*, **20**, 1241 (1948). See Figs. 2, 4.

[5] H. H. Anderson, THIS JOURNAL, **72**, 2091 (1950).

[6] (Added in proof) Since submission of this paper, C. Eaborn, *J. Chem. Soc.*, 3084 (1950) has described Me_2SiI_2 as boiling at 170.0°. The method herein is shorter.

[1] Diesters of pentaerythritol (but not containing nitro-groups in the acid radicals) are known: Barth and Burrell, U. S. Patent 2,356,745 (*C. A.*, **39**, 223 (1945)); Orthner and Freyss, *Ann.*, **484**, 131 (1930).

[1a] Derick and Bissell, THIS JOURNAL, **38**, 2478 (1916).

[2] Anderson and Seyfried, *Anal. Chem.*, **20**, 998 (1948); Boekelheide, *et al.*, THIS JOURNAL, **71**, 3303 (1949); E. Bergmann and Pinchas, *Rec. trav. chim.*, **70**, in press (1951).

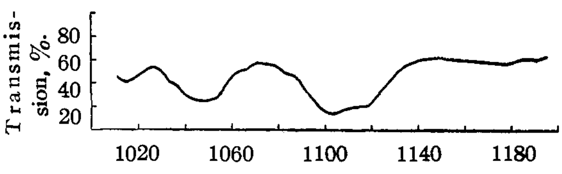

Fig. 1.—Infrared spectrum of (II): 0.045 g. in 1 cc.of chloroform; cell thickness 0.1 mm.

band of the acetal spectrum. This interpretation was confirmed by the investigation of ethyl orthoformate and orthobenzoate (Fig. 2, 3) which absorb in the infrared at similar wave lengths and with a similarly high intensity of the third band (ϵ = molecular extinction coefficient for 1 mole per cc. and 1 mm. cell thickness):

Compound (II): 1178 ($\epsilon = 1 \times 10^4$)–1118[shoulder] (4×10^4)–1103(8×10^{-4})–1048 cm.$^{-1}$(6×10^4); ethyl orthoformate: 1159 ($\epsilon = 2 \times 10^4$)–1125(2.5×10^4)–1092(10×10^4)–1059 cm.$^{-1}$(6×10^4); ethyl orthobenzoate: 1163 ($\epsilon = 1 \times 10^4$)–1108(3.5×10^4)–1081·(6×10^4)–1036 cm.$^{-1}$(4×10^4).

In addition, the spectrum of (II) shows a band at 1015 cm.$^{-1}$, and the spectrum of ethyl orthobenzoate three bands at 1145, 1060 and 1015 (shoulder) cm.$^{-1}$.

Pentaerythritol tetraacetate, which has been studied for comparison, shows in the region investigated, only a single peak, at 1042 cm.$^{-1}$.

It is worthy of note that in contradistinction with the transition from ethers to acetals, the addition, in the ortho-esters, of the third oxygen atom does not cause a splitting of the bands, but only increases considerably the intensity of the third band.

The formation of the ortho-ester (II) is undoubtedly favored by the compactness of its molecule which is evident from a model. It is worth recalling that nitrotrimethylolmethane gives a very similar product (III), on treatment with phosphorus oxychloride.[3]

Esterification of pentaerythritol with p-nitrobenzoyl chloride gives the normal tetra-p-nitrobenzoate, whilst (II) is not attacked by the acid chloride. (II) can, therefore, not be an intermediate in the formation of the tetraester.

Experimental

Pentaerythritol Mono-(p-nitrobenzoate) Ortho-(p-nitrobenzoate) (II).—To a suspension of (I)[4] (15.6 g.) in glacial acetic acid (100 cc.), 4-nitrophenylhydrazine (4.6 g.) and concentrated hydrochloric acid (5 cc.) were added. A clear solution formed which deposited quickly crystals of benzaldehyde 4-nitrophenylhydrazone in quantitative yield (m.p. 189°, after recrystallization). The filtrate was diluted with 100 cc. of alcohol, cooled at 0° and induced to crystallization by scratching with a glass-rod. The compound (II) was washed with methanol and recrystallized from benzene or glacial acetic acid. It formed prisms of m.p. 137–138°; yield 10 g. (80%).

Anal. Calcd. for $C_{19}H_{16}O_9N_2$: C, 54.8; H, 3.9; N, 6.7. Found: C, 54.9; H, 4.1; N, 6.6.

Pentaerythritol Tetra-(p-nitrobenzoate).—A solution of 1.36 g. of pentaerythritol in pyridine was heated at 100° with 7.5 g. of p-nitrobenzoyl chloride for two hours and then poured into cold dilute sulfuric acid. The solid was washed with sodium carbonate solution, water and acetone, and the product (7 g., 95%) recrystallized from glycol monoacetate. It melted at 215°.

Anal. Calcd. for $C_{33}H_{24}O_{16}N_4$: N, 7.6. Found: N, 7.6.

Ethyl orthobenzoate was prepared according to Limpricht[5]; b.p. 131–132° (17 mm.).

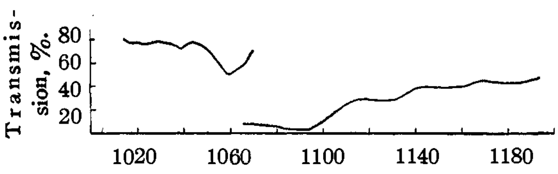

Fig. 2.—Infrared spectrum of ethyl orthoformate: left curve, 0.095 g. in 1 cc. of carbon tetrachloride; right curve, 0.043 g. in 1 cc. of chloroform; cell thickness 0.1 mm.

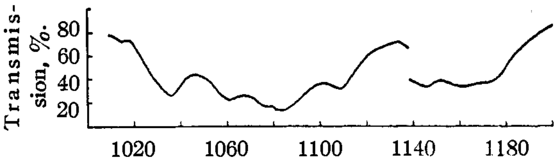

Fig. 3.— Infrared spectrum of ethyl orthobenzoate: left curve, 0.031 g., right curve, 0.092 g. in 1 cc. of carbon tetrachloride; cell thickness 0.1 mm.

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[3] Zetzsche and Zurbruegg, *Helv. Chim. Acta*, **9**, 297 (1926).

[4] Bograchov, This Journal, **72**, 2268 (1950).

[5] Limpricht, *Ann.*, **135**, 87 (1865).

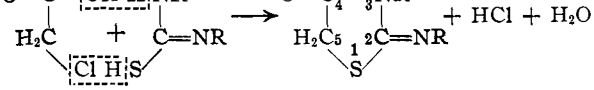
DANIEL SIEFF RESEARCH INSTITUTE
WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL

RECEIVED OCTOBER 26, 1950

The Synthesis of Some 3-Aryl-2-arylimino-4-thiazolidones

BY PRITHWI NATH BHARGAVA

Desai, Hunter and Koppar[1] prepared 3-phenyl-2-phenylimino-4-thiazolidone. The preparation of some 3-aryl-2-arylimino-4-thiazolidones has been reported by Dains, Irvin and Harrel.[2] Klare, Markley and Reid[3] have further studied the conditions for the preparation of this type of compound by condensing diphenylthiourea and monochloroacetic acid in the presence of ethanol and sodium acetate by means of the reaction.



This reaction has now been extended to the synthesis of some 3-aryl-2-arylimino-4-thiazolidones not described as yet in the literature, by the condensation of the corresponding symmetrical diaryl thioureas with monochloroacetic acid in the presence of absolute ethanol and anhydrous sodium acetate. The structure of the thiazolidones is apparent from the method of preparation, and the formation of semicarbazones of the respective compounds gives evidence of the presence of a keto-group. The compounds are listed in Table I.

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[1] Desai, Hunter and Koppar, *Rec. trav. chim.*, **54**, 118 (1935).

[2] Dains, Irvin and Harrel, This Journal, **43**, 613 (1921).

[3] Klare, Markley and Reid, *ibid.*, **52**, 2137 (1930).