the other hand, in the absence of isomerizating conditions, II could react with another triphenylmethyl radical to give a second molecule of triphenylmethane and IV.

Experimental Part

Hexaphenylethane was prepared by reduction of triphenylchloromethane (10 g.) with vanadous chloride by the method of Conant and Scherp.[2] It was collected as a white powder on a büchner funnel in an atmosphere of carbon dioxide, washed with boiled water, drained by suction and a rubber dam, and then dissolved in 250 ml. of purified dioxane which contained 5.6 g. of potassium hydroxide in solution. A nitrogen atmosphere was used. When air was passed through a 25-ml. aliquot of this solution, 0.75 g. of triphenylmethyl peroxide (m.p. 182–184°) precipitated.

A 100-ml. portion of the solution of hexaphenylethane was exposed to sunlight. At the end of three hours the reaction appeared complete, by the change in color from deep yellow to pale greenish yellow and the flask was opened. No precipitate of peroxide formed when air was passed into the flask. The solution was concentrated to 30 ml., then made up to a volume of about 100 ml. with ether, and washed with dilute hydrochloric acid. On evaporation of the ether solution a white crystalline solid separated, which after recrystallization from ethanol weighed 1.254 g. and melted at 142–146°. Further recrystallization raised the melting point to 146–147°. This material was identified as 9-phenylfluorene by a mixed melting point determination with a sample of 9-phenylfluorene prepared by the method of Kliegl.[3] Triphenylmethane (0.898 g., m.p. 85–90°) was isolated from the mother liquors.

Another 100-ml. aliquot was allowed to stand in the dark for four days. At the end of this time air was passed into the solution, and 2.445 g. of triphenylmethyl peroxide (m.p. 185–186°) was obtained. No 9-phenylfluorene or triphenylmethane was found in the filtrate, which was treated as in the previous case. The only crystalline product isolated was a trace (0.012 g.) of triphenylcarbinol, m.p. 160–162°.

For comparison purposes, a sample of the hexaphenylethane (2 g.) was dissolved in 75 ml. of benzene and kept in the dark for 11 days. After aeration the reaction products were worked up as in the dioxane reaction. Only triphenylmethyl peroxide and a trace of ether soluble material were found. From a similar solution which had been exposed to sunlight a few hours, triphenylmethane and 9-phenylfluoryl peroxide, m.p. 194.5–195.5, were obtained. There was no evidence for the presence of 9-phenylfluorene in either case.

---

(2) J. B. Conant and H. W. Scherp, THIS JOURNAL, **53**, 1941 (1931).

(3) A. Kliegl, *Ber.*, **38**, 284 (1905).

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

Dialkyl α-Hydroxyphosphonates Derived from Chloral[1]

BY W. F. BARTHEL, P. A. GIANG AND S. A. HALL

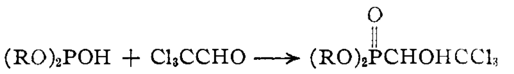
RECEIVED MARCH 20, 1954

As a part of a program on the preparation of candidate insecticides, we made a series of O,O-dialkyl 2,2,2-trichloro-1-hydroxyethylphosphonates, $(RO)_2P(O)CHOHCCl_3$, by condensing chloral with a dialkyl hydrogen phosphite.

Abramov[2] described this condensation reaction, in which he used lithium or sodium methylate as a catalyst for condensing a series of aldehydes or ketones with a dialkyl hydrogen phosphite.

Fields[3] obtained a process patent on the reaction of an aldehyde or ketone with diethyl hydrogen phosphite, using triethylamine as a catalyst to obtain a series of O,O-diethyl α-hydroxyphosphonates.

Craig and Hester[4] condensed chloral and butyl chloral with some phosphite esters, particularly thiocyanoalkyl phosphites, to obtain compounds claimed useful as toxic agents in insecticidal compositions. We found that no catalyst was necessary when the aldehyde used was chloral.



$$(RO)_2POH + Cl_3CCHO \longrightarrow (RO)_2\overset{\displaystyle O}{\overset{\|}{P}}CHOHCCl_3$$

When equimolar quantities of chloral and dialkyl phosphite were mixed, an immediate exothermic reaction took place, which required moderate cooling. Since a catalyst was not added the purification of the final product was simplified. The lower members of the series (below butyl) are solids which were readily purified by recrystallization from appropriate solvents. The liquid dibutyl ester could not be purified by vacuum distillation since appreciable decomposition occurred on heating. The diethyl ester is described in the Fields' patent[3] as a liquid which "decomposes over 100°." We found that the pure diethyl ester is a solid melting at 55–56°. The dimethyl ester[5] has recently attracted interest as an insecticide effective against DDT-resistant house flies.

Dialkylhydrogen Phosphites.—These were prepared from phosphorus trichloride and the appropriate alcohol by the method of McCombie, *et al.*[6] Their physical properties and yields are shown in Table I.

TABLE I

DIALKYL HYDROGEN PHOSPHITES

Phosphite	Yield, %	B.p. °C.	Mm.	$n^{25}D$	Previously reported[7] B.p. °C.	Mm.	$n^{20}D$
Dimethyl	36	63–66	16	1.4005	55–55.5	10	1.4036
Diethyl	80	93	35	1.4057	75	15	1.4080
Dipropyl	65	97	23	1.4150	91.5	11	1.4172
Diisopropyl	55	97	40	1.4057	69.5	9	1.4008
Dibutyl	[8]	122–126	15	1.4220	115	10	1.4240

O,O-Dimethyl 2,2,2-Trichloro-1-hydroxyethylphosphonate.—To 15 g. of chloral (obtained by distilling chloral hydrate over sulfuric acid) was added 11 g. of freshly distilled dimethyl hydrogen phosphite. An immediate vigorous condensation reaction began, as evidenced by a sharp rise in temperature. The reaction mixture was kept below 80° by occasional cooling of the flask under the tap until the main reaction had subsided. The flask was stoppered and held overnight at room temperature. It was chilled in the refrigerator, but taken out from time to time and scratched with a stirring rod until crystallization was in-

---

(1) This work was conducted under funds allotted by the Department of the Army to the Department of Agriculture.

(2) V. S. Abramov, *Doklady Akad. Nauk* (*S.S.S.R.*), **73**, 487 (1950); *J. Gen. Chem.* (*U.S.S.R.*), **22**, 647 (1952).

(3) E. K. Fields, U. S. Patent 2,579,810 (1951).

(4) W. E. Craig and W. F. Hester, U. S. Patent 2,485,573 (1949).

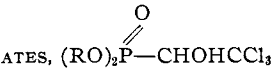
(5) Technical grade O,O-dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate has been designated as "L 13/59" and supplied by R. J. Geary, Bluepoint, N. Y., for entomological tests.

(6) I. H. McCombie, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 380 (1945).

(7) B. A. Arbuzov and V. S. Vinogradova, *Izvestiya Akad. Nauk*, **55**, 620 (1947).

(8) Obtained from Virginia–Carolina Chemical Corporation, Richmond, Va.

TABLE II

O,O-DIALKYL 2,2,2-TRICHLORO-1-HYDROXYETHYLPHOSPHONATES, 
$(RO)_2P(=O)—CHOHCCl_3$

R	Yield, %[9]	M.p., °C.	Formula	Phosphorus, % Calcd.	Phosphorus, % Found	Chlorine, % Calcd.	Chlorine, % Found
CH_3	54	78–80	$C_4H_8Cl_3O_4P$	12.03	12.11	41.32	41.86
C_2H_5	74	55–56	$C_6H_{12}Cl_3O_4P$	10.93	10.96	37.52	37.20
C_3H_7	56	68–70.5	$C_8H_{16}Cl_3O_4P$	10.01	10.00	34.37	34.55
i-C_3H_7	54	105–106.5	$C_8H_{16}Cl_3O_4P$	10.01	10.12	34.37	34.24
C_4H_9	Not purified	Liquid n^{25}_{D} 1.4718	$C_{10}H_{20}Cl_3O_4P$	9.07	9.17	31.14	31.83

duced. The entire mass solidified, giving a quantitative yield of crude product. The crude product, after being crystallized several times from petroleum ether containing a little benzene, melted at 78–80°.

Other dialkyl esters were prepared in the same manner. Their properties, yields and analyses are given in Table II.

---

(9) Yield of recrystallized ester based on dialkyl hydrogen phosphite, Yields of crude product were essentially quantitative for all homologs.

ENTOMOLOGY RESEARCH BRANCH
AGRICULTURAL RESEARCH SERVICE
U. S. DEPARTMENT OF AGRICULTURE
BELTSVILLE, MARYLAND

Detection of Periodate-oxidizable Compounds on Paper Chromatograms[1]

BY R. L. METZENBERG AND H. K. MITCHELL

RECEIVED APRIL 5, 1954

Buchanan, Dekker and Long[2] have reported a method, based on periodate oxidation, for the detection of various glycols and nucleosides on chromatograms. The procedure outlined below is less specific, but is simpler and, in our experience, more sensitive.

Experimental

Preparation of the Chromatogram.—Whatman #1 Filter Paper was used. In some solvent systems, soluble periodate-reacting materials in the paper migrate just behind the solvent front and interfere with the detection of compounds of high R_f value. This problem can be eliminated by washing the paper with the solvent to be used before applying the spots.

Solvent Systems.—Use of phenolic solvents interferes with the sensitivity of the method, as does use of buffered solvents.

Detection of Periodate-oxidizable Compounds.—The chromatogram is dried thoroughly to remove any acid or base remaining after development. It is then sprayed very lightly and evenly with aqueous KIO_4 (0.01 *M*), air-dried at room temperature for 8–10 minutes, and then sprayed with a solution of 35% saturated sodium tetraborate containing 0.8% KI, 0.9% boric acid and 3% soluble starch, boiled to bring the starch into solution.

On areas of the chromatogram not having any periodate-oxidizable substances, periodate reacts with iodide ion to liberate iodine, which in turn gives a blue color with the starch; but wherever periodate has been reduced to iodate ion, iodine is not liberated, and no color is observed. Therefore, white spots are seen on a blue background.

Optimum contrast is usually observed about 10 minutes after the second spraying. The spots are not permanent, but may readily be photographed by interposing the wet chromatogram between two sheets of glass, placing it over a sheet of high contrast printing paper, exposing to light, and developing the print. This has the added advantages of increasing the contrast somewhat, and giving dark spots on a light background.

Discussion.—The specificity seems to be essentially that of the well known periodate reaction.[3] Of compounds tested, tartaric acid, xylose, glucose, sucrose, mannitol, inositol, quinic acid, chlorogenic acid, shikimic acid, glucuronolactone, ascorbic acid, serine, threonine, methionine, cystine, tryptophan, riboflavin, adenosine, guanosine, inosine, xanthosine, cytidine, uridine, catechol, phloroglucinol, gallic acid, β-phenylserine, anthranilic acid and protocatechuic acid show periodate-reducing power. Very weak reactions were given by histidine, tyrosine, aspartic acid, *trans*-cinnamic acid, benzoic acid and *o*-coumaric acid. Compounds which gave no detectable reaction were arginine, ornithine, proline, leucine, isoleucine, lysine, asparagine, glycine, alanine, glutamic acid, Nα-acetylkynurenine, phenylalanine, glutathione, chloromycetin, guanine, hypoxanthine, xanthine, cytosine, uracil, thymine, thymidine, uric acid, mandelic acid, *p*-hydroxybenzoic acid and vanillin.

Anthranilic acid, gallic acid, chlorogenic acid and cystine were observed to give transient yellow or orange colors after the periodate reagent. Malic acid, citric acid and fumaric acid gave dark spots, probably by exceeding the buffer capacity of the second reagent and causing iodate to react with iodide.

Under conditions of optimum sensitivity, the method will give a barely detectable spot with 0.25 μg. of inositol, or its equivalent in periodate reducing power. The limiting factor appears to be the reaction of the periodate with the paper itself.

---

(1) This work was supported in part by a National Science Foundation Predoctoral Fellowship.

(2) J. G. Buchanan, C. A. Dekker and A. G. Long, *J. Chem. Soc.*, 3162 (1950).

(3) E. L. Jackson, "Organic Reactions," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 341.

KERCKHOFF LABORATORIES OF BIOLOGY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

Concerning the Reaction of Lithium, Sodium and Potassium Ethoxide in Ethanol with 2-Ethylhexyl Bromide

BY MELVIN S. NEWMAN AND F. JAMES EVANS, JR.[1]

RECEIVED APRIL 1, 1954

The chemical literature describes many cases in which the variation of the inorganic cation affects the nature of the product or the rate of its formation.[2] We were interested in this aspect of the Williamson reaction, especially with regard to the ratio of ether to olefin formed. It was hoped

---

(1) Taken from the Ph.D. Thesis of F.J.E., 1952.

(2) See O. L. Brady and J. Jakobovits, *J. Chem. Soc.*, 767 (1950), for literature references and discussion.