

Table 5. The reductions of the body weight of pupae of the common housefly in percent through the pupal period.

	Days after pupation					
	1	2	3	4	5	6
Control	100	97.2	96.2	95.4	93.0	—
Abnormal*	100	97.8	97.3	96.2	91.9	—
Abnormal**	100	80.7	66.5	57.8	50.9	47.8

* Adult emerged ** Died in pupal period

の減少が蛹の体内で起っている生化学的、組織学的変化とどのような関係があるかはまだ不明である。

要 約

高槻系イエバエを用いて殺虫剤の効力試験に影響を与えると思われる基礎的な生物学的因子について調査を行ってきたが、その結果について報告する。

1. 幼虫の飼育培基の重さは日経過に伴って減少してゆくが、幼虫の飼育密度とこの培基の減量度との間には指数曲線的関係が認められた。
2. 幼虫の飼育密度が低いと蛹化率、羽化率がやゝ悪くなり、密度が高くなると幼虫期間がやゝ長くなり、蛹の大きさ長さ幅共小となる。
3. 終令幼虫を水あるいは葉液等に浸漬することによる影響として、蛹体重の減少、羽化率の低下が認められ、また早く蛹化したものゝ方が蛹化のおそいものに比して体重も重く、羽化率も高かった。
4. 蛹期間中体重は日経過と共に徐々に減少するが、蛹化第2日目および羽化開始前日の減少が特に著しい。また羽化しないものでは体重の減少が激しく、途中で、羽化するものとはっきり区別されえた。

文 献

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Résumé

In this paper, the writer analyzed the several ecological problems when the larvae of the common housefly, *Musca domestica vicina*, were reared for the biological assay of insecticide. The results are as follows ;

1. The total weight of the breeding medium decreases with elapse of day. With the increase of the larval density the rate of this reduction increases exponentially.
2. At the low larval density the percentages of pupation and emergence become low, and at the high density the larval period elongates and the small pupae appear.
3. The reduction of the pupal body weight and the low percentage of emergence of adult are observed when the third instar larvae were dipped in water or insecticide. Early pupated individuals have more heavy body weight and higher percentage of emergence of adult than the late pupated individuals.
4. During the pupal period, the pupal body weight decreases gradually with the elapse of day, but at the second day after pupation and the day before emergence this reductions are remarkable.

Reaction of Dialkyl β -Dichlorovinyl Phosphates and Their α -Methoxy Derivatives with Sodium *p*-Nitrophenoxide. Studies on Organophosphorus Compounds. III*. Yuji NAGAE, Tomoo WATANABE, Ken'ichi KOJIMA (Institute of Agricultural Chemicals, Toa Agricultural Chemicals Co., Ltd.**) Received July 5, 1958, *Botyu-Kogaku* 23, 115, 1958.

22. Dialkyl β -Dichlorovinyl Phosphate 及びその α -Methoxy 誘導体と Sodium *p*-Nitrophenoxide との反応について 有機燐化合物の研究 第3報 永江祐治・渡辺智夫・小島建一(東亜農薬株式会社 農薬研究所) 33. 7. 5 受理

Dialkyl β -dichlorovinyl phosphate (IV, DDVP 又はその diethyl 体) 及びその α -methoxy 誘導体 (V) に就て β -位の Cl を *p*-nitrophenoxy 基で置換した場合、果して殺虫効果の増強が認

* Part II : *Botyu-Kagaku*, 23, 89 (1958)

** Kozu, Odawara, Kanagawa-ken.

められるか否かを検討する目的の下に本研究を行った。(1) Trialkyl phosphite と methyl trichloroacetate とを反応せしめると初期の報告にある如き dialkyl carbmethoxy-dichloromethyl phosphonate (VI) は得られず, vinyl 構造を有する phosphate (V) を生成することを確認した。(2) 従って V と *p*-nitrophenoxide (VII) との反応によっては勿論文献記載の β -(*p*-nitrophenoxy) 置換 VI (X) は得られない。実験の結果は予期した dialkyl β -chloro- β -(*p*-nitrophenoxy)- α -methoxyvinylphosphate (IX) も得られず, dialkyl *p*-nitrophenyl phosphate (XI, para-oxon 又はその dimethyl 体) が生成することを知った。(3) 同様の反応を IV に就て試みたが同じく XI の生成を認めた。但しこの場合 XI を完全に未反応の IV と分離することは困難であった。(4) 上述の反応における XI の生成は赤外又は紫外吸収スペクトル、ペーパー・クロマトグラフィー等によって確認した。(5) VII の代りに silver *p*-nitrophenoxide を用いても全く同様に XI のみが生成して β -(*p*-nitrophenoxy) 体 (VIII) は得られなかった。(6) V と VII よりは 56% (dimethyl 体) 乃至 80% (diethyl 体) の収率で XI を得るが IV と VII の反応における XI の収率は遙かに低い (11~12%)。 (7) IV と VII による XI の生成についての最適条件を知る為に VII の脱水度と溶媒の影響を調べた。溶媒としてベンゼンを用いる方がエタノールを用いるより良い結果を与え、VII の脱水度は収率に影響しない。尚本反応の機構について簡単に考察を述べた。

Spiess and Spiess¹⁾ reported that dialkyl chloro-carbalkoxy-(*p*-nitrophenoxy)-methyl phosphonates (X) useful as insecticides, were obtained by the treatment of dialkyl carbalkoxy-dichloromethyl phosphonates (VI) with sodium *p*-nitrophenoxide (VII). They prepared VI by the normal Arbuzov reaction of trialkyl phosphites (I) with alkyl trichloroacetates (III). Other workers²⁾ also prepared a series of VI, which were reported to be excellent insecticides with systemic activities. Being interested in the enhancement of insecticidal activity of VI by introducing *p*-nitrophenoxy group, we have studied in details on the above reactions and obtained quite different results from

those mentioned in the literatures.

This paper deals with the unexpected results of the reaction of dialkyl β -dichlorovinyl phosphates (IV) or their α -methoxy derivatives (V) with VII.

As mentioned above, many workers reported that VI was obtained by treating I with III according to the ordinary Arbuzov reaction. But Kharasch et al.⁴⁾ found that this reaction gave dialkyl α -alkoxy- β -dichlorovinyl phosphates (V). They prepared diethyl α -ethoxy- β -dichlorovinyl phosphate ($R=R'=C_2H_5$ in V) from triethyl phosphite and ethyl trichloroacetate. They confirmed the vinyl structure of V ($R=R'=C_2H_5$)

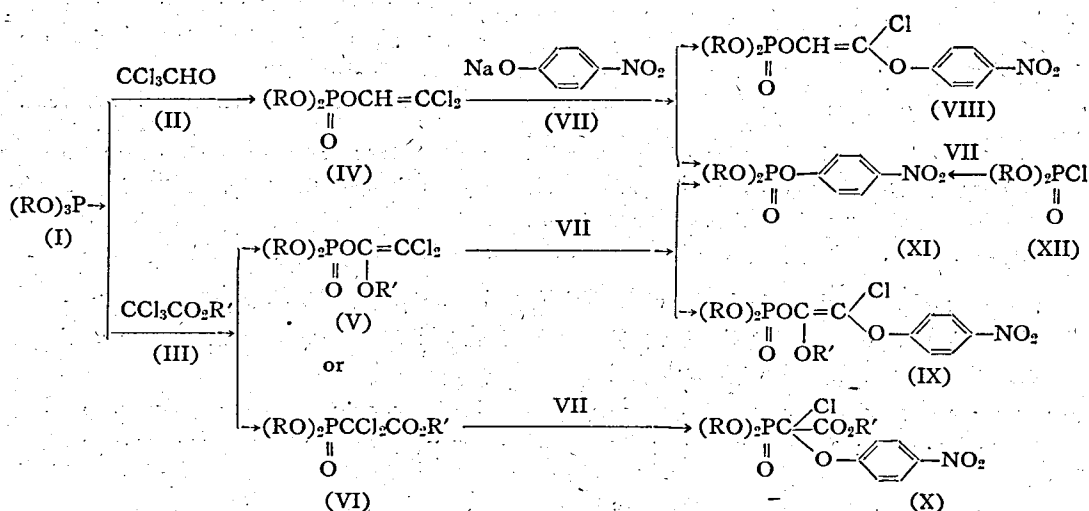


Fig. 1

by infrared absorption data and behavior against acidic hydrolysis.

Similar reaction took place when I was treated with chloral (II) yielding dialkyl β -dichlorovinyl phosphates (IV)^{4,5}. Dimethyl ester of IV (IVa) is an excellent systemic insecticide known as the name of DDVP, which was also obtained by the treatment of dimethyl α -hydroxy- β -trichloroethyl phosphonate (Dipterex) with alkali^{6,7,8}.

It is reasonable that V has high insecticidal effectiveness because of its very similar structure of IV, or dimethyl 1-carbomethoxy-2-propen-2-yl phosphate (Phosdrin, XIII, $R=R'=\text{CH}_3$) as shown in Fig. 2. In Fig. 2, phosphorus atoms of IV, V, XIII and dialkyl *p*-nitrophenyl phosphates (XI) have considerable electropositivity. Relation of biological properties to electronic effect of phosphorus atom has already been discussed by Fukuto⁹, and similar relation was reported by us in the case of azophenyl phosphates¹⁰.

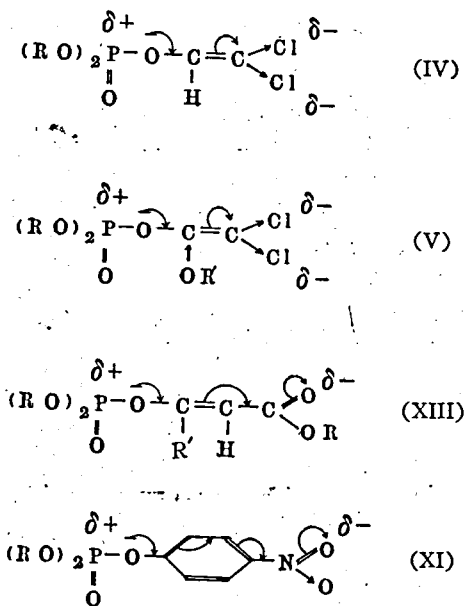


Fig. 2

Shown in Fig. 2, XIII or XI has a group with strong electromeric effect such as carbonyl or nitro conjugated to the double bond linkage. Hence, the phosphorus of XI or XIII seems to have a considerably high electropositivity. Perhaps this is the main reason why XI or XIII

has high effectiveness against insects.

On the contrary, IV or V has only two chlorines in β -position, which cause less electropositivity of phosphorus than that of XI or XIII, owing to the inductomeric effect of chlorine. Moreover, alkoxy group of + inductomeric effect in α -position of V will lessen the electropositivity of phosphorus. From these points of view, IV or V, especially the latter, will be less effective to some extent against insects than XI or XIII.

Reaction of IV or V with VII will afford dialkyl β -chloro- β -(*p*-nitrophenoxy)-vinyl phosphates (VIII) or their α -alkoxy derivatives (IX) respectively. Therefore, it seemed to us that the compounds obtained by Spiess and Spiess were IX instead of X as shown in Fig. 1.

At first we tried to prepare IX according to the description in the literature¹¹. Reaction product (XIV) obtained by the treatment of diethyl α -methoxy- β -dichlorovinyl phosphate (Vb, $R=\text{C}_2\text{H}_5$, $R'=\text{CH}_3$ in V) with VII was purified by the column chromatography or high vacuum distillation. XIV purified by chromatography (fraction A, in Fig. 8) had no chlorine. Fraction B of XIV by distillation also had no chlorine. These results showed that IX or X was not obtained. Fraction A by distillation had about 5% of chlorine owing to the contaminated Vb. Therefore clean-cut separation was done more easily by chromatography than by distillation. Elemental analyses, ultra-violet spectrum and other physical properties such as specific density and refractive index of purified XIV were compared with those of authentic sample of diethyl *p*-nitrophenylphosphate (para-oxon, XIb, $R=\text{C}_2\text{H}_5$ in XI) yielding well agreed results.

Reaction of dimethyl ester of V (Va, $R=R'=\text{CH}_3$) with VII gave dimethyl homolog of XI (XIa, $R=\text{CH}_3$) similarly.

We have continued our investigation on the reaction of IV with VII. Reaction product (XV) of diethyl β -dichlorovinyl phosphonate (IVb, $R=\text{C}_2\text{H}_5$ in IV) with VII was purified by repeated distillations. Data of ultra-violet and infrared spectra and paper chromatography of purified XV were very similar to those of XI (Figs. 5, 6, 7, and 8). However, it had a small content of

chlorine (from 2 to 6%), which was too high to be considered as experimental error.

Purified XV (fraction B) showed characteristic absorption at 1645 cm^{-1} corresponding to double bond linkage ($>\text{C}=\text{C}<$). This suggested that vinyl compound (starting IVb) still remained to some extent. Therefore it seemed that the purified XV by chromatography or distillation was Xib contaminated with a small amount of the starting material, IVb. Calculating the remained IVb in XV (fraction B) from the content of chlorine, IVb amounted to about 20%. Results of elemental analyses of C, H and N agreed with those of the mixture of 20% of IVb and 80% of Xib.

The same result was obtained when IVa was treated with VII. Distillation of reaction product yielded the mixture of 20% of IVa and 80% of XIa.

One of us (K.K.) and his associate also determined the content of IV and XI by bioassay and enzymatic method, and obtained the same result mentioned above.

The experimental results showed that ordinary repeated distillations or chromatography failed to separate XI from IV.

Optimum condition was tried to be found out by the following experiments. In these experiments, content of XI in the crude product, from which main part of unreacted IV was removed at reduced pressure, was determined directly by Aversell and Norris' method¹¹⁾.

VII was used in either thoroughly dried salt or hydrate with 2 moles of water, and benzene or alcohol was used as a solvent. Result is shown in Table 1. Reaction in benzene generally gave better result than in alcohol, but there was no significant difference between dried and hydrated VII.

Having obtained XIb instead of expected VIIIb ($R=C_6H_5$) by the treatment of IVb with VII, we have tried to prepare VIIIb by another method. IVb was treated with silver *p*-nitrophenoxide instead of sodium salt. Two fractions (A and B of XVI) were obtained by repeated distillations. From the result of paper chromatography, it was proved that the reaction also gave unreacted IVb (fraction A) and XIb (fraction B) as shown in Fig. 8.

In Fig. 8, the results of paper chromatography are summarized. Fractions B of XV and XVI gave almost the same R_f values with that of XIb and also gave yellow spots by spraying potassium hydroxide owing to the presence of *p*-nitrophenoxy group. On the contrary, fractions A of XV and XVI gave the same R_f values with IVb and gave no spot by spraying alkali.

This is the strong evidence that fractions A of XV and XVI were IVb and fractions B of them were XIb. However it was failed to detect contaminated IVb in fractions B (about 20%) because of its low sensibility to Hanes-Ischerwood reagent¹².

The authentic sample of XI was prepared by the ordinary method. Diethyl ester (XIb) was obtained in a high yield by the method reported by Fletcher et al¹³. Treatment of VII with diethyl chlorophosphate (XIIIb, $R=C_2H_5$ in XIII) gave unsatisfactory result. On the contrary, dimethyl ester (XIa) was prepared in satisfactory yield by the treatment of VII with dimethyl chlorophosphate (XIIIa, $R=CH_3$ in XIII). XIa was obtained in poor yield by Fletcher's method. In another run, it was tried to prepare XIa by the nitration of dimethyl phenyl phosphate. But the over-all yield from phenol or XIIIa was poor.

The formation of XI by the treatment of IV or V with VII will be explained as shown in Fig. 3.

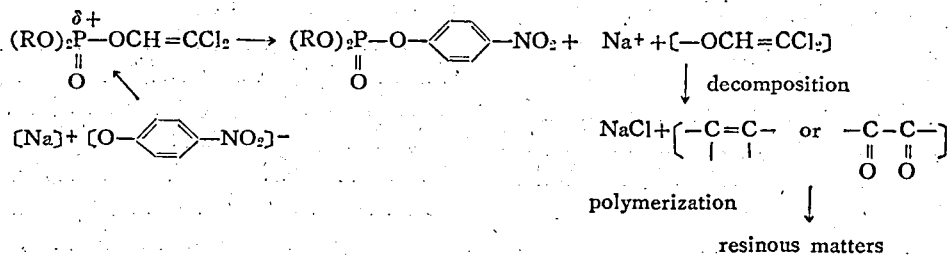


Fig. 3

p-Nitropenoxy group of VII reacts as nucleophilic reagent to the site of electropositively charged phosphorus, and the replacement of β -dichlorovinyl or its α -alkoxy substituted group by *p*-nitrophenoxy group occurs. Eliminated (α -alkoxy-) β -dichlorovinyl groups will be further hydrolysed in alkaline medium to ethylenic or α , β -dicarbonyl compounds which will polymerize to unknown materials. But in the present study, resinous matters obtained as by-product are not yet examined in details.

Experimental

Column chromatography. The reaction products in the following experiments were purified by either high vacuum distillation or column chromatography. Pure XIb was separated from products containing XIb chromatographically with aluminum oxide. But satisfactory results were not obtained in the case of XIa. Owing to the alkalinity of reagent used, XIa was hydrolysed during elution only giving free *p*-nitrophenol and changing color of Al_2O_3 from white to yellow, which suggested the formation of sodium *p*-nitrophenoxide on the surface of Al_2O_3 . Therefore silica gel treated with dilute hydrochloric acid, was used to purify the products containing XIa. Aluminum oxide (*Standardisiert nach Brockman*) and silica gel for chromatographic separation from Merck were used in this experiment.

Partition paper chromatography. Paper chromatography was used as an analytical tool. Ascending development in normal or reversed phase was employed. Toyo Filter Paper No. 50 or No. 51 was used. Solvent systems employed are as follows, and R_f values in each system are given in R_{fx} (No. 50 paper) or $R_{fx'}$ (No. 51 paper).

(a) Normal phase, chloroform-ethanol-water (10:10:6, upper layer). (b) Normal phase, acetic acid-*n*-butanol-water (1:4:5, upper layer). (c) Reversed phase, stationary phase: silicone oil (Silicone KF-54 from Shinetsu Chem. Co.), solvent: chloroform-ethanol-water (10:10:6). (d) Reversed phase, stationary phase: soy bean oil, solvent: 95% ethanol¹⁴. Thus, for example, $R_{fc'}$ shows the R_f value obtained by solvent system c and No. 51 paper. Paper was dipped into 5% ethereal

solution of stationary phase, and dried in the air. Organophosphorus compounds were detected by spraying Hanes-Ischerwood reagent¹⁵ and ultraviolet irradiation. Compounds containing *p*-nitrophenoxy group were detected by spraying 5% alcoholic potassium hydroxide¹⁵. No. 51 paper was more suitable than No. 50 for separation of XIb from IVb, and system c gave the most satisfactory result in general.

Sodium *p*-nitrophenoxide (VII). Anhydrous VII was prepared by heating hydrated VII with 2 moles of water at 110^{°16}.

Preparation of methyl trichloroacetate (IIIa, R = CH₃ in III). IIIa was prepared by the esterification of trichloroacetic acid with absolute methanol using conc. sulfuric acid as catalyser instead of hydrogen chloride⁴. Bp₁₂ 70–71[°] (in 80–94% yield).

Preparation of dialkyl β -dichlorovinyl phosphates (IV).

IV was prepared by the treatment of trialkyl phosphite with chloral⁴. Dimethyl ester (IVa): bp₁ 84[°], n_D^{20} 1.4554, d_4^{20} 1.4223. Anal. Calcd. for $\text{C}_4\text{H}_7\text{Cl}_2\text{O}_4\text{P}$: C, 21.73; H, 3.19; Cl, 32.08; P, 14.03. Found: C, 21.52; H, 3.19; Cl, 32.10; P, 14.30. R_{fc} 0.72, 0.94. I.R. is given in Fig. 6 (A). Diethyl ester (IVb): bp₁ 100[°], n_D^{20} 1.4498, d_4^{20} 1.2973. Anal. Calcd. for $\text{C}_6\text{H}_{11}\text{Cl}_2\text{O}_4\text{P}$: C, 28.93; H, 4.45; Cl, 28.47; P, 12.45. Found: C, 29.18; H, 4.41; Cl, 29.06; P, 12.35. U.V.: in Fig. 5 (C). I.R.: in Fig. 6 (B). R_{fc} 0.47; $R_{fc'}$ 0.53; $R_{fd'}$ 0.89.

Preparation of dialkyl α -methoxy- β -dichlorovinyl phosphate (V). V was prepared from I and IIIa similarly as reported by Kharasch et al⁴.

Dimethyl ester (Va): bp₁ 102–3[°] (in 28% yield). Anal. Calcd. for $\text{C}_7\text{H}_9\text{Cl}_2\text{O}_5\text{P}$: Cl, 28.25. Found: Cl, 28.53. Diethyl ester (Vb): bp_{0.6} 117–121[°] (in 58–61% yield). Anal. Calcd. for $\text{C}_9\text{H}_{13}\text{Cl}_2\text{O}_5\text{P}$: Cl, 25.41. Found: Cl, 25.51. U.V.: in Fig. 5 (A). I.R.: in Fig. 6 (C).

Preparation of dialkyl *p*-nitrophenyl phosphates (XI) Dimethyl ester (XIa). (a) Dimethyl chlorophosphate (XIIa, 144.5 g, 1 mole) was added dropwise into the suspension of thoroughly dried and finely pulverized VII (161 g, 1 mole) in benzene (800 cc) under external cooling. After adding XIIa, the mixture was stirred at reflux for 4 hrs. Red

solid (VII) disappeared, and white solid appeared gradually. After cooling to the room temperature, the reaction mixture was filtered to remove sodium chloride, and the filtrate was washed with 2.5% sodium carbonate (50 cc $\times$ 3) and with water (50 cc $\times$ 3). After drying over sodium sulfate, benzene solution was concentrated to remove solvent yielding pale yellow oil (195–221 g, in 79–89% yield of XIa, 98–99% purity by Averell and Norris' method). A part of this oil was distilled in vacuo for analysis. $Bp_{0.4}$ 167–171°, n_D^{20} 1.4905, d_4^{20} 1.3893, R_{fC} 0.64. Anal. Calcd. for $C_8H_{10}NO_6P$: C, 38.87; H, 4.08; N, 5.67. Found: C, 38.75; H, 4.06; N, 5.75. I.R.: in Fig. 7 (D).

(b) The mixture of equimolar amount (0.05 moles) of *p*-nitrophenol, XIIa and sodium carbonate was stirred at reflux for 3 hrs. Main part of *p*-nitrophenol was recovered, and XIa was obtained in poor yield (20–35%).

(c) Sodium phenoxide (0.3 moles) was treated similarly as described in (a) with XIIa yielding 22.5 g of dimethyl phenyl phosphate (XVIII, $bp_{1.5}$ 115–130°, in 37.2% yield). XVIII (20.0 g, 0.1 mole) was nitrated with the mixture of conc. nitric acid (90 g) and glacial acetic acid (45 cc) at 0–10°. Distillation of crude product gave 10.3 g of XIa (in 41.7% yield). Over-all yield of XIa from phenol or XIIa was 15.5%.

Diethyl ester (XIb). (a) The mixture of equimolar amount (0.1 mole) of *p*-nitrophenol, diethyl chlorophosphate (XIb) and sodium carbonate was treated similarly as described in (b) of XIa. Crude product of 98–99% purity was obtained in the almost quantitative yield. Analytical sample was distilled in vacuo for two times. Bp_1 169–170°, n_D^{20} 1.5030, d_4^{20} 1.2839, R_{fB} 0.99, R_{fC} 0.58, $R_{fC'}$ 0.69, R_{fD} 0.92. Anal. Calcd. for $C_{10}H_{14}NO_6P$: C, 43.64; H, 5.13; N, 5.09. Found: C, 43.46; H, 5.08; N, 5.11. U.V.: in Fig. 5 (B). I.R.: in Fig. 7 (E).

Reaction of Vb with VII. Vb (65 g) was added dropwise into the suspension of dried VII (37.5 g) in ethanol (200 cc). After adding Vb, the mixture was stirred at reflux for 4 hrs. After cooling to the room temperature, reaction mixture was filtered to remove sodium chloride. The filtrate was concentrated in vacuo to remove ethanol. Any

volatile components were removed by heating on the boiling water bath at 0.1 mm Hg. Viscous oil (XIV, 89 g) was obtained.

A part (5 g) of XIV was purified by column chromatography as shown in Fig. 4.

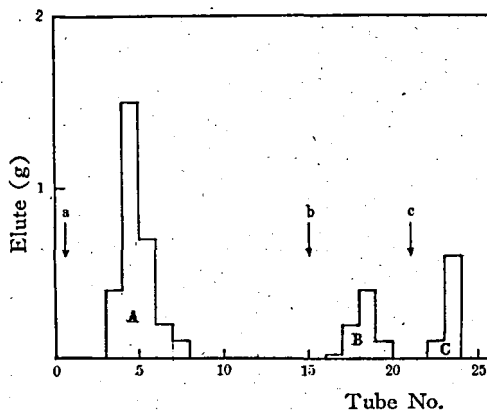


Fig. 4. Column chromatogram of XIV.

Five grams of XIV was treated. Absorbant: Al_2O_3 . Arrows (→) shows that the sample was eluted with: (a) ether, (b) ether-methanol (90:10), and (c) ether-methanol (80:20). Each tube contains 10 cc.

Three fractions were obtained.

Fraction A: Colorless oil, 2.9 g (80.5% yield of XIb based on Vb, found P, 11.26; Cl, 0.80; N, 5.05, R_{fA} 0.99, R_{fB} 0.98). Fraction B: 0.7 g. Fraction C: 0.7 g.

Fractions B and C were resinous matters which gradually solidified on standing, but they are not examined further. U. V. of A: in Fig. 5 (B). Another part of XIV (25 g) was dissolved in ether, washed with dil. sodium carbonate and water, and dried over sodium sulfate. Ether was evaporated, and the residue was distilled in vacuo for 2 times yielding two fractions.

Fraction A: The mixture of unreacted Vb (ca. 20%) and XIb (ca. 80%), 6.9 g ($bp_{0.01-2}$ 144–151°, in ca. 34% yield of XIb, n_D^{20} 1.4996, d_4^{20} 1.2817, found P, 11.06; Cl, 4.79).

Fraction B: Pure XIb, 6.4 g ($bp_{0.01-2}$ 148–51°, in 40% yield of XIb; n_D^{20} 1.5035, d_4^{20} 1.2839. Found P, 11.26; Cl, 0).

Reaction of Va with VII. Va (5.3 g) was similarly treated with VII (3.4 g) as described in the reaction of Vb with VII. Crude product (5.4 g)

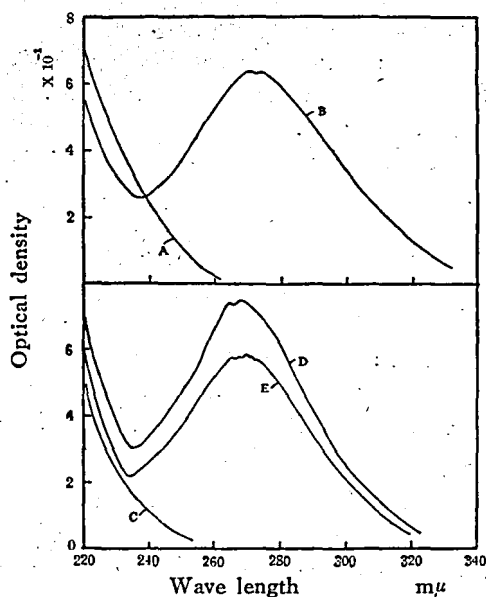


Fig. 5. Ultra-violet spectra.

- A: Diethyl α -methoxy- β -dichlorovinyl phosphate (Vb).
 B: Diethyl *p*-nitrophenyl phosphate (XIb) and fraction A of XIV.
 C: Diethyl β -dichlorovinyl phosphate (IVb).
 D: Fraction B of XVII.
 E: Fraction B of XV.

Optical densities were observed at the concentration of 25 γ of substance per ml. of 95% ethanol in silica cell of 10mm width.

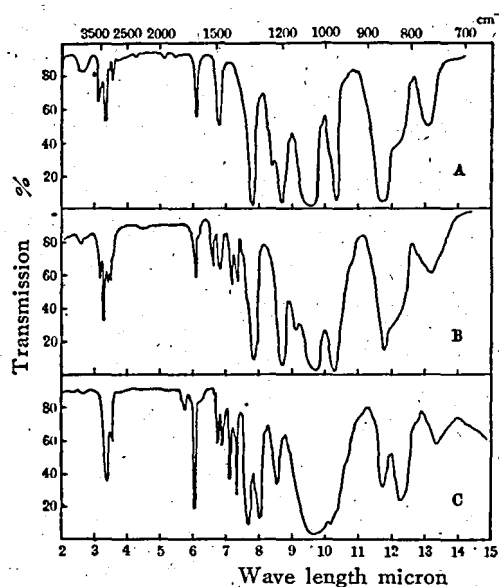


Fig. 6. Infrared spectra.

- A: Dimethyl β -dichlorovinyl phosphate (IVa).
 B: Diethyl β -dichlorovinyl phosphate (IVb).
 C: Diethyl α -methoxy- β -dichlorovinyl phosphate (Vb). (Pure liquid, instrument: Koken Model D 301).

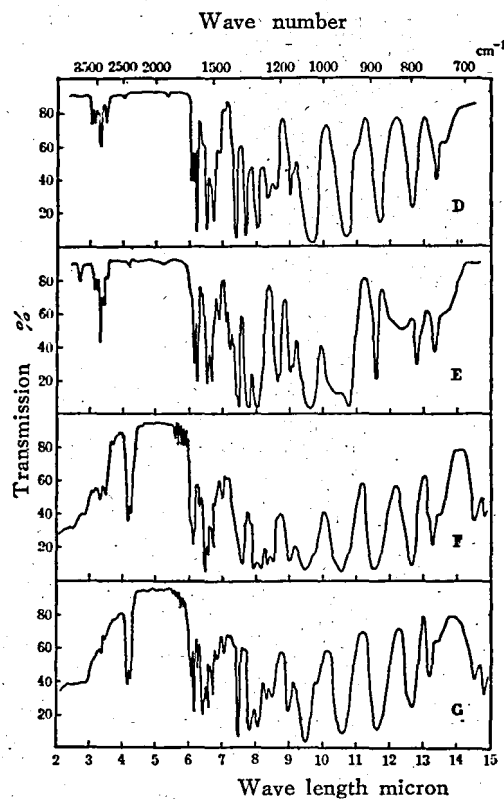


Fig. 7. Infrared spectra.

- D: Dimethyl *p*-nitrophenyl phosphate (XIa).
 E: Diethyl *p*-nitrophenyl phosphate (XIb).
 F: Fraction B of XVII.
 G: Fraction B of XV.

(Pure liquid, instruments: Koken Model D 301 for D and E, Perkin Elmer Model 112 for F and G).

was purified chromatographically with silica gel giving XIa (2.8 g, in 56% yield of XIa, n_D^{20} 1.4905, d_4^{20} 1.3895, found P, 12.60; N, 5.65; Cl, 0).

Reaction of IVb with VII. IVb (24.7 g) was treated similarly as Vb with VII (16.1 g) in benzene. Reaction mixture was decanted to separate benzene layer from tarry matters, which were discarded. Crude product (XV) obtained from benzene layer, was distilled repeatedly in vacuo.

Fraction A: Unreacted Vb, 7.1 g (bp_{0.4-0.6} 71-5°, 35% of starting Vb, n_D^{20} 1.4514, d_4^{20} 1.2961, R_{fC} 0.55, $R_{fC'}$ 0.59, R_{fD} 0.89, found C, 30.00; H, 4.76; Cl, 28.49; N, 0.71; mol. wt. 226).

Fraction B: The mixture of IVb (ca. 20%) and

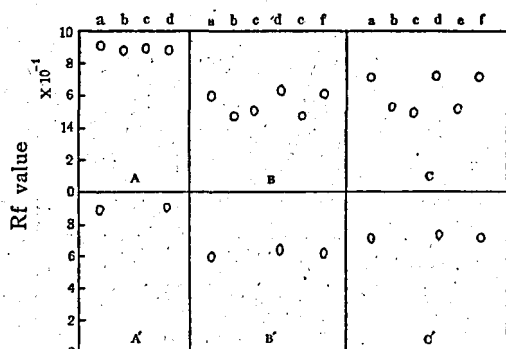


Fig. 8. Partition paper chromatograms.

- a: Diethyl *p*-nitrophenyl phosphate (XIb).
 b: Diethyl β -dichlorovinyl phosphate (IVb).
 c: Fraction A of XV.
 d: Fraction B of XV.
 e: Fraction A of XVI.
 f: Fraction B of XVI.

A, B and C were sprayed with Hanes-Ischerwood reagent, and radiated with UV lamp. A', B' and C' were sprayed with 5% alcoholic potassium hydroxide.

A and A': System d and No. 51 paper.

B and B': System c and No. 50 paper.

C and C': System c and No. 51 paper.

XIb (ca. 80%), 3.1 g (bp_{0.5} 158–162°, in 11% yield of XIb, n_D^{20} 1.4912, d_4^{20} 1.2820, R_{fc} 0.63, $R_{fc'}$ 0.71, $R_{fd'}$ 0.90, found C, 41.74; H, 5.02; Cl, 5.83; N, 4.07, mol wt. 275). U.V.: in Fig. 5 (E). I.R.: in Fig. 7 (G).

In another run, XV was purified chromatographically on Al₂O₃ yielding XIb of ca. 93% purity (found C, 42.57; H, 5.06; Cl, 2.07).

Reaction of IVb with silver *p*-nitrophenoxide.

IVb (12.5 g) was treated with silver *p*-nitrophenoxide (13.2 g, prepared by double decomposition between VII and silver nitrate) similarly as with VII. Two fractions were obtained by repeated

distillations of crude product (XVI).

Fraction A: Unreacted IVb (bp_{0.002-5} 65–69, 5.6 g or 45% of starting IVb, found Cl, 28.88, R_{fc} 0.45, $R_{fc'}$ 0.51).

Fraction B: Impure XIb (bp_{0.02-3} 130–5°, 1.1 g or 8.5% yield of XIb R_{fc} 0.60, $R_{fc'}$ 0.70).

Reaction of IVa with VII. IVa (22.1 g) was treated with VII (16.1 g) similarly as described in the reaction of IVb with VII. Crude product (XVII) was twice distilled in vacuo.

Fraction A: Unreacted IVa, 7.4 g (bp_{0.6} 80–82°, 33% recovery of starting IVa, n_D^{20} 1.4528, d_4^{20} 1.4223, $R_{fc'}$ 0.71, 0.96, found Cl, 32.16; P, 14.31).

Fraction B: The mixture of IVa (ca. 20%) and XIa (ca. 80%), 3.7 g (bp_{0.4} 152–5°, in 12% yield of XIa, n_D^{20} 1.5058, d_4^{20} 1.3966, $R_{fc'}$ 0.64, found C, 35.93; H, 3.71; Cl, 6.13; P, 13.17).

U.V.: in Fig. 5 (D). I.R.: in Fig. 7 (F).

Determination of content of XI in the reaction product of IV with VII. The reaction product

obtained by the treatment of IVa or IVb with dried or hydrated VII in alcohol or benzene was heated on the boiling water bath at 0.1–0.01 mm Hg to remove main part of unreacted IV. Content of XIa or XIb was determined by Averell and Norris' method.

Calibration curves were prepared with authentic samples of XIa and XIb. Content of XIa or XIb was calculated from the following equations,

$$\text{For XIa: } y = 343x + 3.69$$

$$\text{For XIb: } y = 312.7x + 0.36$$

(x is observed optical density, and y is dosage of XI, γ/ml).

The result is given in Table 1.

Table 1. Determination of content of XI in the reaction product of IV with VII.

Mols. of IV and VII	IV used	Form of VII	Solvent	Yield of crude product (A) g	Content of XI in A %	Total yield of XI from IV %
0.05	IVa	anhydrous	benzene	4.2	XIa 71.3	24
0.05	IVa	hydrate	benzene	1.6	XIa 73.5	28
0.05	IVa	anhydrous	ethanol	1.8	XIa 22.2	3.3
0.05	IVa	hydrate	ethanol	1.6	XIa 42.7	5.5
0.25	IVb	anhydrous	benzene	90.0	XIb 37.5	24
0.1	IVb	hydrate	benzene	15.6	XIb 35.0	20
0.05	IVb	anhydrous	ethanol	3.4	XIb 34.6	9
0.05	IVb	hydrate	ethanol	3.3	XIb 45.8	11

Summary

(1) Dialkyl α -methoxy- β -dichlorovinyl phosphates (V) were prepared by the treatment of trialkyl phosphites with methyl trichloroacetate. Their vinyl structures were confirmed from infrared absorption data.

(2) V was treated with sodium *p*-nitrophenoxide (VII) in order to prepare β -(*p*-nitrophenoxy) derivatives of V (IX). But the reaction gave only unexpected dialkyl *p*-nitrophenyl phosphates (XI) instead of IX or dialkyl chloro-(*p*-nitrophenoxy)-carbomethoxy-methyl phosphonate (X, $R' = CH_3$) which was reported in the earlier literature.

(3) Reaction of dialkyl β -dichlorovinyl phosphates (IV) with VII also gave XI. However, in this case, it was very difficult to remove starting IV contaminated in XI.

(4) The formation of XI in the above reactions (Summary 2 and 3) was confirmed from the data of ultraviolet and infrared spectra, partition paper chromatography and physical properties such as specific density and refractive index.

(5) Reaction of IV with silver *p*-nitrophenoxide failed also to give IX. It gave XI similarly as VII did.

(6) The yield of XI from V and VII was 56% (in dimethyl ester) or 80% (in diethyl ester) respectively. Reaction of IV with VII gave poorer yield than V, namely 11–12% in dimethyl and diethyl esters.

(7) Optimum condition was tried to be found out in the reaction of IV with VII. Reactions in benzene gave better result (from 20 to 28% yield of XI) than those in alcohol (from 3 to 11% yield of XI). Dried or hydrated VII gave no significant difference to the yield of XI.

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