[Chem. Pharm. Bull. 25(2) 231—238 (1977)]

UDC 541.64.04 : 547.361.2-11.04

Studies on Telomers and Oligomers of Vinylene Carbonate. VI.[1] Stereoselective Conversion of Vinylene Carbonate Telomers to *trans* Unsaturated Phosphate Esters and Their Chemical Behaviors

Naoki Mitsuo, Takehisa Kunieda, and Takeo Takizawa

Faculty of Pharmaceutical Sciences, University of Tokyo[2]

(Received May 19, 1976)

Smooth conversion of telomers of vinylene carbonate with carbon tetrachloride or methylene bromide as a telogen to novel *trans* enol phosphates, and the reactivities of the phosphates thus formed are described. Both *trans*-"*anti*"-*trans*- and *trans*-"*syn*"-*trans*-isomers of the $n=2$ telomers, 5-chloro-5′-trichloromethyl-(4,4′-bi-1,3-dioxolan)-2,2′-dione and 5-bromo-5′-dibromomethyl-(4,4′-bi-1,3-dioxolan)-2,2′-dione gave, on treatment with trialkyl phosphites, the identical *trans* dialkyl 2-(5-trichloromethyl- and 2-(5-dibromomethyl-2-oxo-1,3-dioxolan-4-yl)vinyl phosphates in good yields, without any detectable amount of *cis* isomer and the phosphonate, while the $n=1$ adduct failed to give the corresponding enol phosphate. Stereospecific conversion of the phosphate to *cis* 2-(5-trichloromethyl-2-oxo-1,3-dioxolan-4-yl)vinyl acetate was readily achieved by new vinylic exchange reaction catalyzed by palladium chloride in acetic acid by way of the processes, *trans* oxypalladation and *trans* deoxypalladation. Reactions involving catalytic hydrogenation, chlorination with titanium chloride and conversion to α,β-unsaturated aldehydes are summarized in Chart 2.

Keywords——vinylene carbonate telomers; enol phosphate; enol acetate; Perkow reaction; vinylic exchange reaction; photo reduction; catalytic reduction; trichloromethyl group

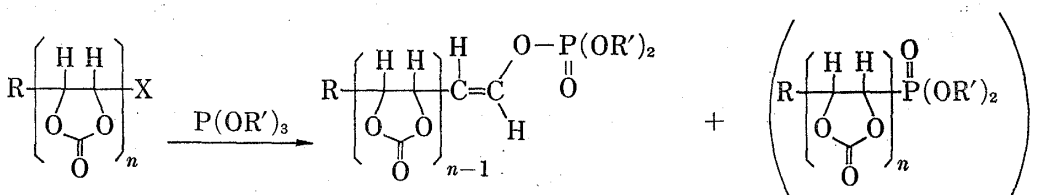
Recent investigations in our laboratories of the free radical telomerization of vinylene carbonate have revealed the novel and facile synthetic routes to natural and unnatural aldosugars,[3] indicative of high potential of this type of reaction as synthetic tools for carbohydrates.

This paper deals with the smooth conversion of telomers of vinylene carbonate with carbon tetrachloride and methylene bromide[4] to novel *trans* enol phosphate esters which may be served as "synthon" for deoxy sugar derivatives, and the reactivities of the phosphates thus formed. The Perkow reaction may provide the general route to such enol phosphates from α-halocarbonyl compounds[5] which are, however, hardly accessible in the synthetic fields of carbohydrates.

There has been reported the reaction of monochloroethylene carbonate with trialkyl phosphites to give the nearly equal amounts of the unsubstituted vinyl phosphates (**2**) ($n=1$, R=H) and the phosphonates **3** ($n=1$, R=H) as the Arbuzov reaction products.[6] This reaction was applied to the type **1** telomers ($n=1$, 2).

Thus, vinylene carbonate telomers (**1**) ($n=2$, R=CCl_3, $CHBr_2$),[4] both chloro- and bromo-compounds, on treatment with trialkyl phosphites in the aprotic solvents, benzene, toluene

1) Part V: K. Hosoda, T. Kunieda, and T. Takizawa, *Chem. Pharm. Bull.* (Tokyo), **24**, 2927 (1976).
2) Location: *Hongo, Bunkyo-ku, Tokyo.*
3) H. Takahata, T. Kunieda, and T. Takizawa, *Chem. Pharm. Bull.* (Tokyo), **23**, 3017 (1975); For a review, T. Kunieda and T. Takizawa, *J. Syn. Org.* (Japan), **33**, 560 (1975).
4) T. Tamura, T. Kunieda, and T. Takizawa, *J. Org. Chem.*, **39**, 38 (1974).
5) *cf.*) F.W. Lichtenthaler, *Chem. Rev.*, **1961**, 607.
6) H. Gross, G. Engelhardt, J. Freiberg, W. Bürger, and B. Costisella, *Liebigs Ann. Chem.*, **707**, 35 (1967); R. C. D. Selms and T. W. Lin, *J. Org. Chem.*, **32**, 2023 (1967).

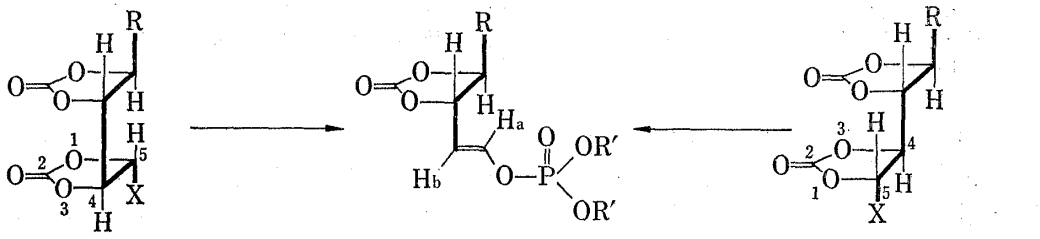


1 ($n=1, 2, 3\cdots$) 2 3

(R=H, CCl_3, $CHBr_2$; X=Cl, Br)

and dioxane, afforded the corresponding *trans* enol phosphates (2) in high stereoselectivity without any practical amounts of *cis*-isomers and the phosphonates (3) ($n=2$), in contrast with the $n=1$ adducts (1) (R=CCl_3), from which any product could not be identified except a trace of the hydrolyzed trichloro-α-hydroxypropionaldehyde in dimeric form.[7] Generality of this reaction was further disclosed by the recent observation on the similar transformation of the $n=3$ telomers (R=CCl_3) into the enol phosphate esters (2) ($n=3$).[8]

Thus, stereoisomeric telomers (**4a** and **4b**), whose stereochemistry was previously established as "*syn*"- and "*anti*"-forms respectively,[3] reacted with two equimolar triethyl- (or trimethyl-) phosphite in boiling toluene to give the identical unsaturated phosphate (**5**) in 85% (65%) and 80% (72%) yields, respectively. The use of benzene and dioxane as the solvents in place of toluene sharply decreased the yields of **5** (R′=C_2H_5) from **4a** to 25% and 14%, respectively. Similar treatment of the bromo compounds,[4] **6a** (*syn*) and **6b** (*anti*), which were thermally less stable than the corresponding chloro derivatives, afforded in benzene 46% and 56% yields of the same type of enol phosphate (**7**), respectively.



syn form *anti* form

4a : R=CCl_3, X=Cl **5** : R=CCl_3, R′=CH_3, C_2H_5 **4b** : R=CCl_3, X=Cl

6a : R=$CHBr_2$, X=Br **7** : R=$CHBr_2$, R′=C_2H_5 **6b** : R=$CHBr_2$, X=Br

Ultraviolet (UV)-irradiation of the phosphate (**5**) in tetrahydrofuran[9] resulted in the smooth formation (80% yield) of the enol phosphate (**19**) having dichloromethyl group which could be regarded as the protected aldehyde.[3,10]

Spectral data of the products (**5**, **7**, and **19**), which all showed vicinal coupling constants ($J_{a,b}$) of —12 Hz due to olefinic protons and distinct absorptions at —955 cm^{-1} in the nuclear-magnetic resonance (NMR) and infrared (IR) spectra (Table I), strongly support *trans* stereochemistry with respect to the double bond.[6]

Among the plausible mechanisms for such highly stereoselective formation of *trans*-isomers, a mechanism involving direct attack of the phosphites on the terminal carbonate ring at C_5 or O_1 position where electron-density is relatively lower, might be considered[11] besides the

7) T. Matsuura, T. Kunieda, and T. Takizawa, *Chem. Pharm. Bull.* (Tokyo), **25**, 239 (1977).
8) Y. Nii, T. Kunieda, and T. Takizawa, *Tetrahedron Letters*, **1976** 2323 (1976).
9) N. Mitsuo, T. Kunieda, and T. Takizawa, *J. Org. Chem.*, **38**, 2255 (1973).
10) *cf.*) B.M. Trost, M.J. Bogdanowicz, and J. Kern, *J. Am. Chem. Soc.*, **97**, 2218 (1975).
11) High stereoselectivity in the present conversion may cast some insight into the mechanistic details which will be the subject of the future publication.

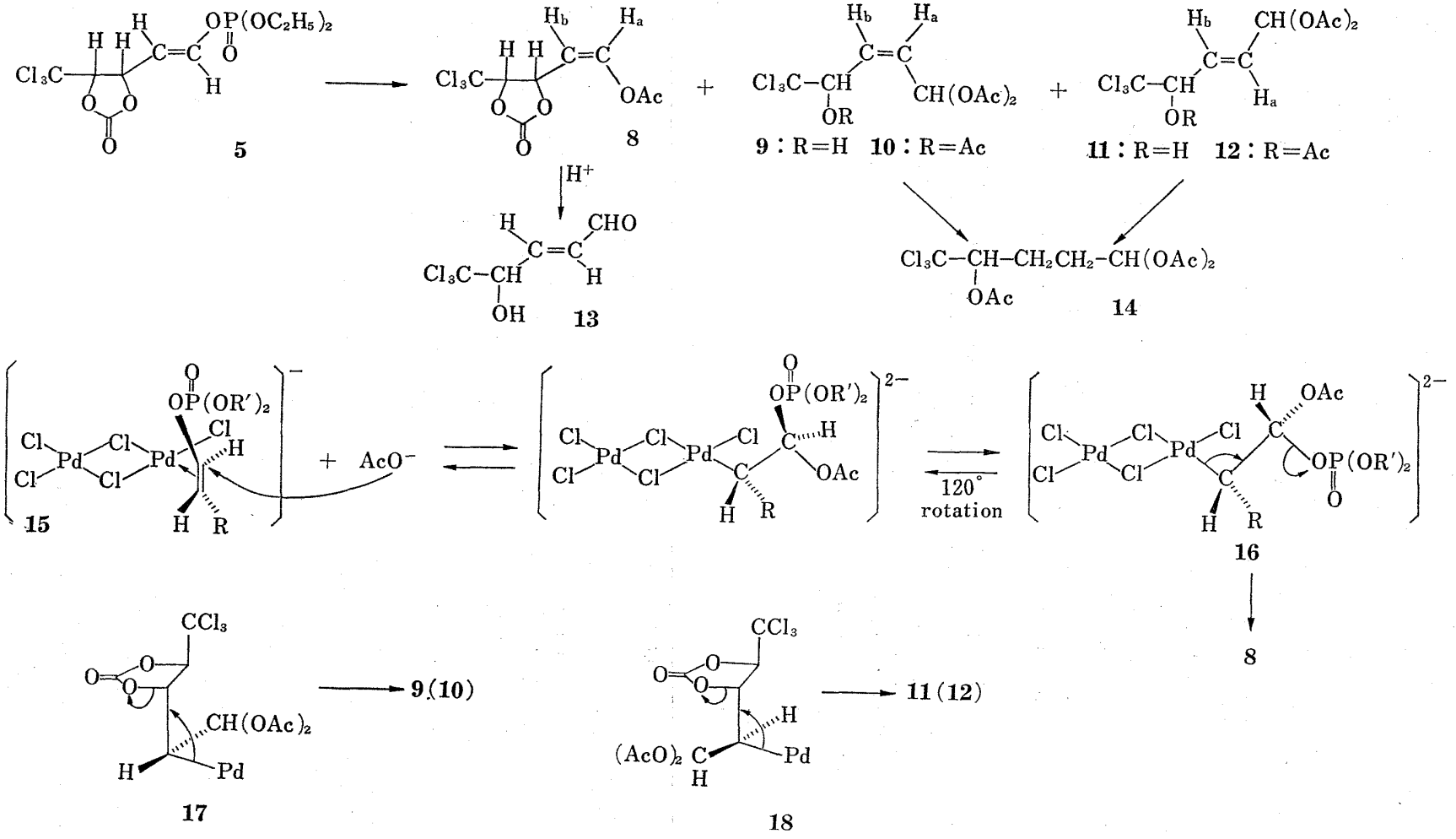


Chart 1

reported one which involves the initial formation of chloroethylene oxide followed by rearrangement to chloroacetaldehyde postulated as the key intermediates.[6]

Conversion of the phosphate (**5**) to the enol acetate (**8**), more sensitive towards nucleophiles, was readily achieved by new vinylic exchange reaction catalyzed by palladium (II) in acetic acid,[12] while considerable difficulties were encountered in the cleavage of the vinyl-phosphate bond under hydrolytic conditions. Thus, acetic acid solution of **5** was treated with catalytic amounts of palladium chloride in the presence of lithium chloride and lithium acetate at room temperature to give rise to *cis* enol acetate (**8**) stereospecifically as major product in addition to the migrated olefines, *cis*- and *trans*-2-pentene diacetates (**9** and **11**). Elevated temperature (40—100°) in the reaction resulted in higher yields of *trans* derivatives (**11** and **12**) in the compensation of **8** and **9**.

Acid hydrolysis of **8** gave α,β-unsaturated aldehyde (**13**) ($J_{a,b}$=15.0 Hz) with double bond migration, and acetylation of **9** and **11** to the triacetates (**10** and **12**) followed by catalytic hydrogenation over palladium–carbon gave the identical pentane derivative (**14**) exclusively.

Stereochemistry with the olefinic bonds of compounds (**8**, **9** (**10**) and **12** (**11**)), was established as *cis*, *cis*, and *trans*, respectively, on the basis of spectral data shown in Table I.

Table I. Spectral Data for Unsaturated Phosphates and Acetates

Compound	$J_{a,b}$ (Hz)	IR (cm^{-1})
5 ($R'=C_2H_5$)	12.0	955
5 ($R'=CH_3$)	12.0	960
7	12.0	945
19	11.0	955
8	6.0	
9	(10.5)[a]	
10	11.0	
12	15.5 (16.0)[a]	

a) 2,4-dinitrophenylhydrazones

Palladium(II)-catalyzed vinylic exchange may involve attack of acetate anion on a dimeric palladium (II) π-complex (**15**) from outside the coordination sphere to give σ-bonded intermediate (**16**) as demonstrated in the similar system.[12] This type of addition suggests *trans* stereochemistry and the subsequent deoxypalladation step to give transvinylation product[13] must occur in *trans* fashion by the principle of microscopic reversibility. Thus *trans*-oxypalladation followed by *trans*-deoxypalladation could account for the exclusive formation of *cis* isomer (**8**). *gem*-Diacetates (**9** and **11**) would be secondarily formed from the probable precursor (**8**) *via* palladium-coordinated σ-complexes like **17** and **18**.

Enol phosphate (**5**) underwent hydrogenolysis in absolute ethanol over Adams catalyst at 1 atm pressure of hydrogen with exclusive formation of 4-ethyl-5-trichloromethyl-1,3-dioxolan-2-one (**20**), presumably through the initial product vinyldioxolanone,[14] while the saturated phosphate ester (**21**) was the sole product when palladium on carbon was used as catalyst in ethyl acetate. These behaviors are consistent with the observations previously described.[14,15]

Reaction with metallic zinc in methanol followed by chromatography on silica gel gave exclusively the conjugated aldehyde (**23**) which was formed *via* non-conjugated phosphate (**22**) whose intermediacy was shown by the smooth allylic rearrangement of the isolated **22** to **23**

12) *cf.*) P.M. Henry, *Accounts Chem. Res.*, **6**, 16 (1973); P.M. Maitlis, "The Organic Chemistry of Palladium," Vol. II, Academic press, New York, 1971, p. 109.
13) A. Sabel, J. Smidt, R. Jira, and H. Prigge, *Chem. Ber.*, **102**, 2939 (1969).
14) *cf.*) A. Jung and R. Engel, *J. Org. Chem.*, **40**, 3652 (1975).
15) H.I. Jacobson, M.J. Griffin, and E.V. Jensen, *J. Am. Chem. Soc.*, **79**, 2068 (1957).

on acid treatment. Treatment with titanium tetrachloride (at 25°) and stearic anhydride (at 140°) gave **24** (98%) tentatively assigned and **25** (19%), respectively.

Smooth formation of enol phosphates from vinylene carbonate telomers described herein would provide a new route to biologically important classes of compounds, sugar-phosphates involving nucleotides and lipids.[16]

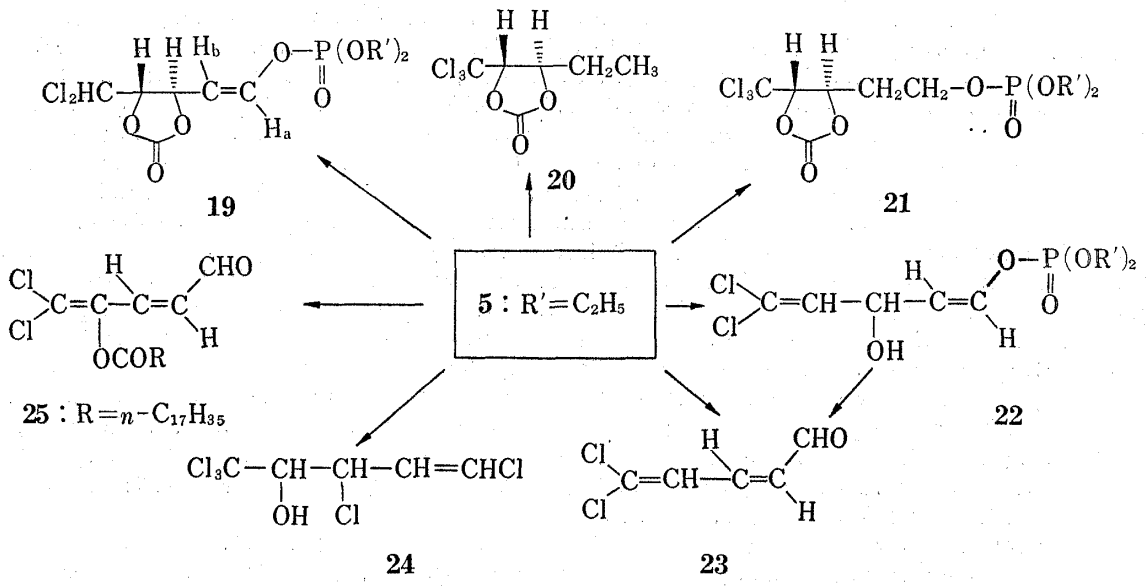


Chart 2

Experimental

The melting points are uncorrected. NMR spectral data were obtained using a JEOL PS-100 NMR spectrometer, and are reported in δ (ppm downfield from TMS) and J(Hz). IR spectra were taken on a JASCO DS-402G IR spectrophotometer. Vinylene carbonate telomers, 5-chloro-5′-trichloromethyl[4,4′-bi-1,3-dioxolan]-2,2′-dione (**4a, b**) and 5-bromo-5′-dibromomethyl[4,4′-bi-1,3-dioxolan]-2,2′-dione (**6a, b**) were prepared by the reported method.[4]

Diethyl 2-(5-Trichloromethyl-2-oxo-1,3-dioxolan-4-yl)vinyl Phosphate (5: R′=C_2H_5)——a) From **4a**: Telomer (**4a**) (0.35 g, 1.08 mmol) and triethyl phosphite (0.35 g, 2.11 mmol) were dissolved in toluene (12.5 ml), and the solution was refluxed for 24 hr under nitrogen atmosphere. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel (methylene chloride) to give the crystalline enol phosphate (**5**) (0.24 g, 59%) in addition to the recovery of **4a** (0.11 g). Recrystallization from *n*-hexane/benzene or carbon tetrachloride gave **5** as colorless prisms: mp 87—88°; IR (KBr) 3000, 1875, 1670, 1260, 1150, 955 cm^{-1}; NMR ($CDCl_3$) δ 1.40 (6H, t, J=7), 4.20 (4H, d-q, J_1=7, J_2=7), 4.95 (1H, d, J=4), 5.15 (1H, d-d, J_1=9, J_2=4), 5.60 (1H, d-d, J_1=12, J_2=9), 6.95 (1H, d-d, J_1=12, J_2=8). *Anal.* Calcd. for $C_{10}H_{14}O_7Cl_3P$: C, 31.32; H, 3.68. Found: C, 31.40; H, 3.66.

b) From **4b**: The toluene solution (28 ml) of telomer (**4b**) (1.0 g, 3.07 mmol) and triethyl phosphite (1.0 g, 6.02 mmol) was refluxed under nitrogen atmosphere for 24 hr. The solvent was removed *in vacuo*, and the residue was chromatographed on silica gel (methylene chloride) to give **5** (0.92 g, 78%) in addition to the small amount of **4b** (0.025 g). The IR spectrum (KBr) and melting point were identical with those of the specimen prepared from **4a**.

Dimethyl 2-(5-Trichloromethyl-2-oxo-1,3-dioxolan-4-yl)vinyl Phosphate (5: R′=CH_3)——a) From **4a**: In the analogous manner described for **5** (R′=C_2H_5), this phosphate was prepared in 65% yield (0.177 g) from telomer (**4a**) (0.25 g, 0.77 mmol) and trimethyl phosphite (0.319 g, 3.15 mmol). Recrystallization from carbon tetrachloride gave analytical sample as colorless prisms, mp 114°; IR (KBr) 3040, 2980, 1820, 1670, 1460, 1370, 1270, 1153, 1050, 998, 945 cm^{-1}; NMR ($CDCl_3$) δ 3.85 (6H, d, J=11), 4.85 (1H, d, J=4), 5.15 (1H, d-d, J_1=9, J_2=4), 5.65 (1H, d-d, J_1=12, J_2=9), 6.95 (1H, d-d, J_1=12, J_2=8). *Anal.* Calcd. for $C_8H_{10}O_7Cl_3P$: C, 27.03; H, 2.84. Found: C, 27.33; H, 2.88.

16) *cf.*) N. Mitsuo, T. Kunieda, and T. Takizawa, Abstracts, 96th Annual Meeting of Pharmaceutical Society of Japan, Nagoya, April, 1976, II-p 68.

b) From **4b**: Analogously to the procedure described for **5** ($R'=C_2H_5$), telomers (**4b**) (3.17 g, 10 mmol) and trimethyl phosphite (4.96 g, 40 mmol) gave 72% yield (2.49 g) of the enol phosphate **5** ($R'=CH_3$), which was identical with the specimen obtained above with regard to the IR spectrum and melting point.

Diethyl 2-(5-dibromomethyl-2-oxo-1,3-dioxolan-4-yl)vinyl Phosphate (7)——a) From **6a**: A solution of telomer (**6a**) (0.45 g, 1.06 mmol) and triethyl phosphite (0.35 g, 2.11 mmol) in benzene was refluxed for 48 hr under nitrogen stream. After removal of the solvent *in vacuo*, the product was purified by silica gel column chromatography (methylene chloride) to give the crystalline enol phosphate (**7**) (0.212 g, 46%). Recrystallization from carbon tetrachloride/*n*-hexane gave colorless crystals, mp 55—56°; IR (KBr) 2980, 1810, 1670, 1265, 1160, 960 cm^{-1}; NMR ($CDCl_3$) δ 1.40 (6H, t, $J=7$), 4.20 (4H, d-q, $J_1=7.5$, $J_2=7.5$), 4.70 (1H, d-d, $J_1=5$, $J_2=4$), 5.15 (1H, d-d, $J_1=9$, $J_2=5$), 5.60 (1H, d-d, $J_1=12$, $J_2=9$), 5.85 (1H, d, $J=4$), 6.90 (1H, d-d, $J_1=12$, $J_2=7.5$). *Anal.* Calcd. for $C_{10}H_{15}O_7Br_2P$: C, 27.42; H, 3.45. Found: C, 27.53; H, 3.46.

b) From **6b**: A solution of *anti* isomer (**6b**) (0.235 g, 0.55 mmol) and triethyl phosphite (0.180 g, 1.08 mmol) in benzene (10 ml) was refluxed under nitrogen atmosphere for 2 days. The solvent was removed *in vacuo*, and the residue was chromatographed on silica gel (methylene chloride/acetone) to afford the starting material **6b** (0.021 g) and the enol phosphate (**7**) (0.142 g, 56%). The IR spectrum of the product (mp 55—56°) recrystallized from carbon tetrachloride was identical with that of the sample prepared above.

2-(5-Trichloromethyl-2-oxo-1,3-dioxolan-4-yl)vinyl Acetate (8)——To the glacial acetic acid solution (10 ml) of the enol phosphate (**5**) ($R'=C_2H_5$, 0.77 g, 2.01 mmol) were added palladium chloride (0.042 g), lithium acetate (0.066 g), and lithium chloride (0.083 g). After stirring for 3 days at room temperature the solvent was removed *in vacuo* below 40°. The residue was poured in water, and extracted with methylene chloride. Evaporation of the extracts *in vacuo* followed by the silica gel chromatography (methylene chloride/acetone) gave oily *cis*-enol acetate (**8**) (0.150 g, 26%) in addition to the starting material (**5**) (0.335 g). The acetate has the following physical properties; IR (neat) 3110, 3000, 1830, 1770, 1675, 1375, 1200 cm^{-1}; NMR ($CDCl_3$) δ 2.20 (3H, s), 4.90 (1H, d, $J=4$), 5.20 (1H, d-d, $J_1=8.5$, $J_2=6$), 5.55 (1H, d-d, $J_1=8.5$, $J_2=4$), 7.45 (1H, d, $J=6$): mass Calcd. for $C_8H_7O_5Cl_3$: M, 288, M+2 290, M+4 292, M+6 294 (27: 27: 9: 1). Found: M, 288, M+2 290, M+4 292, M+6 294 (27: 27: 9: 1).

5,5,5-Trichloro-4-hydroxy-2-pentenal (13)——The enol acetate (**8**) (0.118 g, 0.41 mmol) was dissolved in 50% methanol (10 ml) which contained conc. hydrochloric acid (0.1 ml), and heated at 85° for 1 hr. Extraction with methylene chloride followed by column chromatography on silica gel (methylene chloride/acetone) gave an oily product (**13**) (0.007 g, 8%): IR (neat) 3300, 2850, 1690 cm^{-1}; NMR ($CDCl_3$) δ 4.40 (1H, d, $J=5.5$, disappeared when D_2O was added), 4.95 (1H, t, $J=4.5$), 6.60 (1H, d-d, $J_1=15$, $J_2=7$), 7.70 (1H, d-d. $J_1=15$, $J_2=4$), 9.65 (1H, d, $J=7$).

***cis*-1,1-Diacetoxy-5,5,5-trichloro-2-penten-4-ol (9)**——The mixture of **5** (5.5 g, 14.4 mmol), palladium chloride (1.0 g, 5.6 mmol), lithium chloride (2.0 g, 47 mmol) and lithium acetate (1.6 g, 24 mmol) in ethyl acetate (40 ml) containing acetic acid (5 ml) was kept below 20° under stirring for 2 days. Removal of the solvent gave red oily residue which was extracted with methylene chloride. The extracts were evaporated *in vacuo*. The residue was chromatographed on silica gel (benzene/methylene chloride) to give **8** (1.2 g, 29.4%), **9** (1.3 g, 29.6%) and **11** (0.13 g, 3%) in the recovery of the unchanged **5** (0.65 g, 12%).

Diacetate (**9**): Recrystallization from *n*-hexane/benzene gave colorless prisms, mp 110—112°, IR (nujol) 3480, 1770, 1680, 955 cm^{-1}, NMR ($CDCl_3$) δ 2.10 (6H, s), 5.10 (1H, d, $J=7$), —5.9 (2H, m), 7.50 (1H, d, $J=8$). *Anal.* Calcd. for $C_9H_{11}O_5Cl_3$: C, 35.35; H, 3.60. Found: C, 35.10; H, 3.56.

Triacetate (**10**): Recrystallization from *n*-hexane/benzene gave colorless prisms, mp 64—65°, IR (Nujol) 1760 cm^{-1}, NMR ($CDCl_3$) δ 2.08 (3H, s), 2.10 (3H, s), 2.16 (3H, s), 5.81 (1H, d-d, $J_1=11$, $J_2=8$), 5.98 (1H, d-d, $J_1=11$, $J_2=7$), 6.28 (1H, d, $J=8$), 7.57 (1H, d, $J=7$). *Anal.* Calcd. for $C_{11}H_{13}O_6Cl_3$: C, 37.99; H, 3.74. Found: C, 37.91; H, 3.68.

2,4-Dinitrophenylhydrazone of **9**: Yellow-orange needles from *n*-hexane/methylene chloride, mp 145—147°, IR (KBr) 3540, 3400, 3260, 1618, 1595 cm^{-1}, NMR ($CDCl_3$) δ 3.20 (1H, br. s), 5.10 (1H, d, $J=7$), 6.12 (1H, d-d, $J_1=10.5$, $J_2=7$), 6.62 (1H, t, $J=10.5$), 7.93 (1H, d, $J=10$), 8.30 (1H, d, $J=10.5$), 8.30 (1H, d-d, $J_1=10$, $J_2=2$), 9.07 (1H, d, $J=2$), 11.19 (1H, br. s.). *Anal.* Calcd. for $C_{11}H_9O_5N_2Cl_3$: C, 34.44; H, 2.37; N, 14.61. Found: C, 34.61; H, 2.31; N, 14.84. The compounds (**8** and **11**) were identical with *cis* enol acetate (**8**) and *trans*-2-penten-4-ol (**11**) prepared separately and characterized with respect to the IR and the NMR spectra.

***trans*-1,1-Diacetoxy-5,5,5-trichloro-2-penten-4-ol (11) and *trans*-1,1,4-Triacetoxy-5,5,5-trichloro-2-pentene (12)**——The mixture of **5** (1.0 g, 2.6 mmol), palladium chloride (0.13 g, 0.7 mmol) and sodium acetate (0.5 g, 6 mmol) in acetic acid (10 ml) was stirred at 50° for 2 days. The low boiling materials were removed *in vacuo* and the residue was washed with methylene chloride. The washings were evaporated and the products were purified by chromatography on silica gel (benzene/methylene chloride) to give **11** (0.5 g, 59%) and **12** (0.24 g, 26%) as major products.

Diacetate (**11**): Oil, IR (neat) 3360, 1750 cm^{-1}, NMR ($CDCl_3$) δ 2.12 (6H, s), 4.71 (1H, d, $J=3$), —6.25 (2H, m), 7.20 (1H, d, $J=4$). Acetyfation with acetic anhydride in pyridine gave triacetate which was identical with **12** prepared above.

Triacetate (**12**): Oil, IR (neat) 1765 cm^{-1}, NMR ($CDCl_3$) δ 2.08 (6H, s), 2.20 (3H, s), 5.90 (1H, d, $J=6$), 6.0 (1H, d-d, $J_1=15.5$, $J_2=4$), 6.20 (1H, d-d, $J_1=15.5$, $J_2=6$), 7.14 (1H, d, $J=4$).

2,4-Dinitrophenylhydrazone of **12**: Orange prisms from ethanol, mp 143—145°, IR (Nujol) 3300, 1760, 1608 cm^{-1}, NMR ($CDCl_3$) δ 2.27 (3H, s), 6.08 (1H, d, $J=6$), 6.38 (1H, d-d, $J_1=16$, $J_2=6$), 6.88 (1H, d-d, $J_1=16$, $J_2=8.5$), 7.91 (1H, d, $J=8.5$), 8.00 (1H, d, $J=10$), 8.45 (1H, d-d, $J_1=10$, $J_2=2.5$), 9.18 (1H, d, $J=2.5$). *Anal.* Calcd. for $C_{13}H_{11}O_6N_4Cl_3$: C, 36.66; H, 2.59; N, 13.16. Found: C, 36.95; H, 2.58; N, 13.21.

2,5,5-Triacetoxy-1,1,1-trichloropentane (14)——Triacetate (**12**) (0.2 g) in ethyl acetate was hydrogenated in the presence of 10% Pd-C (0.1 g) under 1 atm hydrogen at room temperature overnight. The product was purified by chromatography on silica gel (benzene/methylene chloride) to give **14** (0.16 g) as an oil, IR (neat) 1765 cm^{-1}, NMR ($CDCl_3$) δ 2.12 (6H, s), 2.22 (3H, s), 1.73—2.20 (4H, m), 5.56 (1H, d-d, $J_1=9$, $J_2=3$), 6.88 (1H, t, $J=4.5$).

On the same treatment as above, *cis*-triacetate (**10**) also gave the saturated compound (**14**).

2,4-Dinitrophenylhydrazone: Yellow needles from ethanol, mp 143—145°, IR (Nujol) 3450, 3280, 1750, 1625, 1590 cm^{-1}, NMR ($CDCl_3$) δ 2.21 (3H, s), 2.50 (4H, m), 5.68 (1H, d-d, $J_1=8$, $J_2=2$), 7.62 (1H, t, $J=4.5$), 7.95 (1H, d, $J=10$), 8.40 (1H, d-d, $J_1=10$, $J_2=2.5$), 9.16 (1H, d, $J=2.5$). *Anal.* Calcd. for $C_{13}H_{13}O_6N_4Cl_3$: C, 36.49; H, 3.04; N, 13.10. Found: C, 36.56; H, 3.07; N, 12.94.

Diethyl 2-(5-dichloromethyl-2-oxo-1,3-dioxolan-4-yl)vinyl Phosphate (19)——The tetrahydrofuran solution (20 ml) of the trichloromethyl compound (**5**) (0.77 g, 1.30 mmol) was irradiated in a quartz vessel with a high-pressure mercury lamp for 5 hr. After removal of the solvent the residue was chromatographed on silica ge (methylene chloride/acetone) to give the crystalline dichloromethyl compound (**19**) (0.365 g, 80%). Recrystallization from carbon tetrachloride gave **19** as colorless prisms, mp 68—69°; IR (KBr) 2990, 1803, 1670, 1265, 1163, 955 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (6H, t, $J=7$), 4.25 (4H, d-q, $J_1=7.5$, $J_2=7.5$), 4.75 (1H, t, $J=4.5$), 5.25 (1H, d-d, $J_1=8.5$, $J_2=4.5$), 5.60 (1H, d-d, $J_1=11$, $J_2=8$), 6.00 (1H, d, $J=4.5$), 6.95 (1H, d-d, $J_1=11$, $J_2=7.5$). *Anal.* Calcd. for $C_{10}H_{15}O_7Cl_2P$: C, 34.41; H, 4.33. Found: C, 34.26; H, 4.26.

5-Trichloromethyl-4-ethyl-1,3-dioxolan-2-one (20)——A solution of the enol phosphate (**5**) ($R'=C_2H_5$, 0.248 g, 0.65 mmol) in absolute ethanol (20 ml) was shaken in the presence of platinum oxide (20 mg) under 1 atm hydrogen for 5 min. After decantation the solvent was removed below 30° *in vacuo*. The product was purified by column chromatography on silica gel (benzene) to give **20** as an oily compound (0.065 g, 43%): IR (neat) 2965, 1830, 1470, 1373, 1170 cm^{-1}: NMR ($CDCl_3$) δ 1.10 (3H, t, $J=7$), 1.90 (2H, m), 4.70 (2H, m); mass Calcd. for $C_6H_7O_3Cl_3$: M, 232, M+2 234, M+4 236, M+6 238 (27: 27: 9: 1). Found: M, 232, M+2 234, M+4 236, M+6 238 (27: 27: 9: 1).

Diethyl 2-(5-Trichloromethyl-2-oxo-1,3-dioxolan-4-yl)ethyl Phosphate (21)——Enol phosphate (**5**) ($R'=C_2H_5$, 0.77 g, 2.01 mmol) was dissolved in ethyl acetate (15 ml), and 10% palladium on carbon (0.2 g) was added. Catalytic hydrogenation was continued under 1 atm hydrogen for 20 hr. The catalyst was filtered off, and evaporation of the solvent gave **21** (0.755 g, almost quantitative) as an oily product, which was purified by silica gel chromatography using methylene chloride/acetone as an eluting solvent: IR (neat) 2995, 1825, 1265, 1165 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (6H, t, $J=7$), 2.35 (2H, q, $J=6$), 4.20 (6H, m), 4.95 (1H, t-d, $J_1=6$, $J_2=4$), 5.10 (1H, d, $J=4$).

5,5-Dichloro-2,4-pentadienal (23)——a) To a methanolic solution of **5** ($R'=C_2H_5$, 1.0 g, 2.61 mmol) was added zinc dust (2.0 g), and the mixture was vigorously stirred at room temperature for 4 hr. The solvent was removed *in vacuo*, and the residue was chromatographed on silica gel (methylene chloride/acetone) to give **23** (0.070 g, 18%) as colorless oil: IR (neat) 1685, 1620, 1575, 1290, 1220, 1165, 1115, 980, 910; NMR ($CDCl_3$) δ 6.25 (1H, d-d, $J_1=7$, $J_2=15$), 6.75 (1H, d, $J=11$), 7.30 (1H, d-d, $J_1=11$, $J_2=15$), 9.60 (1H, d, $J=7$). 2,4-Dinitrophenylhydrazone was prepared in the usual way, and recrystallized from ethanol to give analytical sample as dark red crystals, mp 173°. *Anal.* Calcd. for $C_{11}H_8O_4N_4Cl_2$: C, 39.90; H, 2.44; N, 16.92. Found: C, 40.11; H, 2.47; N, 16.69.

b) The mixture of **5** ($R'=C_2H_5$, 0.5 g, 1.30 mmol) and zinc (1.0 g) in methanol was vigorously stirred at room temperature for 4 hr. The insoluble materials were filtered off and the filtrate was evaporated *in vacuo* to leave an oily residue which was extracted with methylene chloride. Evaporation of the extracts gave the unconjugated diene (**22**) (0.24 g, 61%) as an oil, which showed the following spectral data; IR (neat) 3400, 2990, 1690, 1635, 1250, 1040 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (6H, t, $J=7$), 3.50 (1H, s, disappeared when D_2O was added), 4.25 (4H, d-q, $J_1=7.5$, $J_2=7.5$), 5.00 (1H, d-d, $J_1=8$, $J_2=7$), 5.55 (1H, d-d, $J_1=12$, $J_2=7$), 6.00 (1H, d, $J=8$), 6.75 (1H, d-d, $J_1=12$, $J_2=7$). The phosphate (**22**) (0.24 g, 0.79 mmol) thus formed was dissolved in 90% methanol (5 ml) containing 1 drop of conc. hydrochloric acid. After standing at room temperature for 2 hr, the solution was refluxed for 0.5 hr. Removal of the solvent gave an oily residue, whose IR spectrum was identical with that of the authentic dienone (**23**) prepared above.

1,3,5,5,5-Pentachloro-1-penten-4-ol (24)——A solution of the enol phosphate (**5**) ($R'=C_2H_5$, 0.38 g, 1 mmol), titanium tetrachloride (0.38 g, 2 mmol) and methanol (0.1 ml) in methylene chloride (5 ml) was stirred at room temperature for 15 hr. Then it was poured into cold water (6 ml), and acetic acid was added. The methylene chloride layer was separated and evaporated *in vacuo*. Purification of the residue by silica gel chromatography (methylene chloride) gave oily product (**24**) (0.25 g, quantitative yield), which was acetylated with acetic anhydride in pyridine to give the acetate, bp 50°/3 mmHg, IR (neat) 3080, 2970, 1770, 1625, 1430, 1380, 1215, 1100 cm^{-1}; NMR ($CDCl_3$) δ 2.20 (3H, s), 5.90 (1H, m), 6.15 (3H, m). *Anal.* Calcd. for $C_7H_7O_2Cl_5$: C, 27.99; H, 2.35; Cl, 59.01. Found: C, 27.96; H, 2.28; Cl, 59.09.

5,5-Dichloro-4-stearoyloxy-2,4-pentadienal (25)——The mixture of enol phosphate (**5**) ($R'=C_2H_5$, 0.384 g, 1 mmol), stearic anhydride (0.550 g, 1 mmol), and sodium stearate (0.306 g, 1 mmol) was heated at 140° without any solvent for 4 hr. Chromatography of the reaction mixture on silica gel using benzene as an eluting solvent gave **25** (0.048 g, 11%) as an analytically pure sample in addition to the unchanged (**5**) (0.16 g), mp 64—66°; IR (KBr) 2890, 1770, 1680, 1612, 1570, 1470, 1385, 1095, 970 cm^{-1}; NMR ($CDCl_3$) δ 0.75 (3H, t, $J=6$), 1.25 (30H, m), 2.55 (2H, t, $J=7$), 6.10 (1H, d-d, $J_1=15$, $J_2=7$), 7.40 (1H, d, $J=15$), 9.60 (1H, d, $J=7$). *Anal.* Calcd. for $C_{23}H_{38}O_3Cl_2$: C, 63.73; H, 8.84. Found: C, 63.65; H, 8.87.