Pentacovalent Phosphorus. I. Reactions of Dimethylketene Dimers with Tertiary Phosphites[1]

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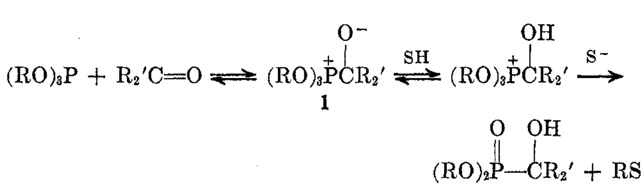
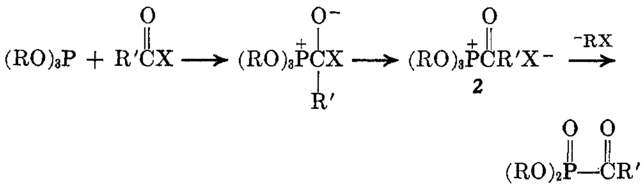
Studies of the reactions of the dione **3** and lactone **4** dimers of dimethylketene with a series of trialkyl phosphites and with dimethyl methylphosphonite have been carried out. The reactions of **4** give generally a carboalkoxy enol phosphite **9**, whereas the dione **3** reactions yield either **9** or a carboalkoxyl oxophosphonite **8** depending on the phosphite used. Tri-*n*-butylphosphine effects the isomerization of **3** to **4**. These results are explained in terms of a suggested series of reactions which includes formation of a five-membered ring pentacovalent phosphorus intermediate in an unusual ring expansion involving the postulated initial product of phosphorus attack on carbonyl carbon of **3** or **4**.

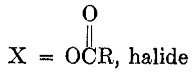
Simple unsubstituted dialkyl and diaryl ketones are generally unreactive[3] toward tertiary phosphites except at temperatures above 170°[4] unless the initial adduct **1** can be trapped by protonation.[5] Alternatively, the intermediate **1** can be trapped and lead to ultimate product if one of the groups attached to carbonyl carbon is an easily displaced substituent (X in **2**).



$$(RO)_3P + R_2'C{=}O \rightleftharpoons \underset{\mathbf{1}}{(RO)_3\overset{+}{P}\overset{O^-}{\overset{|}{C}}R_2'} \xrightleftharpoons{SH} (RO)_3\overset{+}{P}\overset{OH}{\overset{|}{C}}R_2' \xrightarrow{S^-} (RO)_2\overset{O}{\overset{\|}{P}}-\overset{OH}{\overset{|}{C}}R_2' + RS$$



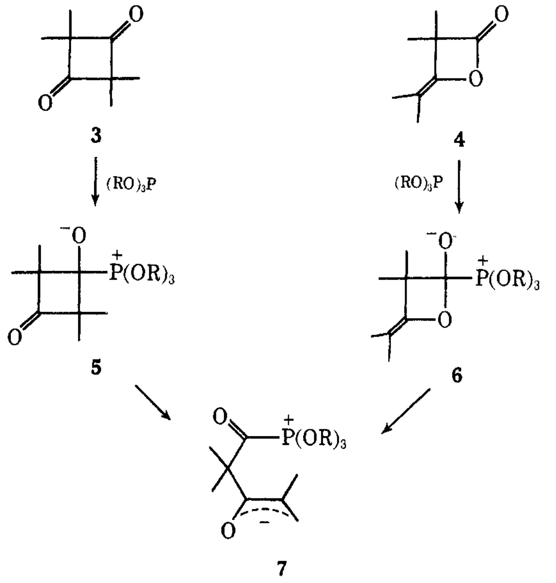
$$(RO)_3P + R'\overset{O}{\overset{\|}{C}}X \longrightarrow (RO)_3\overset{+}{P}\underset{R'}{\overset{O^-}{\overset{|}{C}}}X \longrightarrow \underset{\mathbf{2}}{(RO)_3\overset{+}{P}\overset{O}{\overset{\|}{C}}R'X^-} \xrightarrow{-RX} (RO)_2\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{C}}R'$$



$$X = O\overset{O}{\overset{\|}{C}}R, \text{ halide}$$

Thus acyl halides[6] and acid anhydrides[7] are reactive in this manner.

The departure of the group X might also be expected to be facilitated by ring strain in the reactant carbonyl compound. It therefore seemed probable that the dimers of dimethylketene, 2,2,4,4-tetramethyl-1,3-cyclobutanedione (**3**) and 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid *β*-lactone (**4**), would be reactive toward trivalent phosphorus. These dimers had been found to react readily to give a common ring-opened product with other nucleophiles such as amines, mercaptans, and alcohols.[8] Potentially, phosphites would be expected to give the same one of several conceivable products from either dimer *via* the common intermediate **7** resulting from ring opening of the initial dimer–phosphite adduct **5** or **6**.[9] Surprisingly, distinctly different products were realized from the two dimers in proportions dependent on the nature of the alkoxy groups on phosphorus. We believe the results we report here to be best explained in terms of a novel reaction series in which the incipient phosphonium enolate **7** is trapped *via* ring expansion to a five-membered ring pentacovalent phosphorus intermediate. Although formation of a pentacovalent intermediate from a phosphonium salt is not an uncommon process, its formation *via* a ring expansion is unusual. The ultimate product is postulated as arising from a novel alkoxy migration from phosphorus to carbonyl carbon.



Results

Dione Reactions—Two types of products result from the reaction of phosphites with dione and have the

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[1] Part of this work has been published in preliminary form: W. G. Bentrude and E. R. Witt, *J. Amer. Chem. Soc.*, **85**, 2522 (1963). This work was supported by Public Health Service Grant No. CA-11045 from the National Cancer Institute.

[2] (a) Address correspondence to this author, University of Utah. (b) Taken in part from the Ph.D. Thesis of the W. Delmar Johnson, University of Utah, June 1969. National Institutes of Health Predoctoral Fellow, 1966–1969. (c) University of Utah. (d) Celanese Research Laboratories.

[3] A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, New York, N. Y., 1967, p 60.

[4] A. C. Poshkus and J. E. Herweh, *J. Org. Chem.*, **29**, 2567 (1964).

[5] P. A. Chopard, V. M. Clark, R. F. Hudson, and A. J. Kirby, *Tetrahedron*, **21**, 1961 (1965).

[6] G. Kamai and V. A. Kukhtin, *Khim. Primen. Fosfororg. Soedin. Tr. Konf. 1st 1955*, 91 (1957); *Chem. Abstr.*, **52**, 241*b* (1958).

[7] M. S. Kabachnik and P. A. Rossiiskaya, *Izv. Akad. Nauk SSSR*, 364 (1945).

[8] (a) R. H. Hasek, E. U. Elam, J. C. Martin, and R. G. Nations, *J. Org. Chem.*, **26**, 700 (1961); (b) R. H. Hasek, E. U. Elam, and J. C. Martin, *ibid.*, **26**, 4340 (1961); (c) G. R. Hansen and R. A. DeMarco, *J. Heterocycl. Chem.*, **6**, 291 (1969).

[9] Although the ring opening in the reactions of amines with **3** apparently involves hydrolysis of the four-membered ring Schiff base,[8c] the potential for reaction *via* **7** is evident.

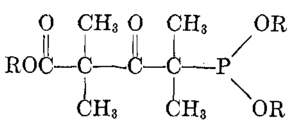
TABLE I

REACTIONS OF DIONE **3** WITH PHOSPHITES AND PHOSPHONITE

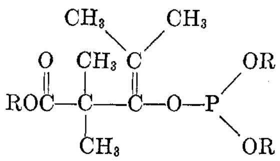
PXYZ			Mol of PXYZ/mol of **3**	Time, hr	*T*, °C	% convn	% yield of **8**	% yield of **9**	% yield of **4**	% yield of other products
X	Y	Z								
OMe	OMe	OMe	2.0	218	120	100[a]	75[a] (33)[b]	15[a] (10)[b]	Trace	
OEt	OEt	OEt	2.0	541	120	80[a]	47[a] (20)	44[a] (20)	Trace	
O-*n*-Pr	O-*n*-Pr	O-*n*-Pr	2.0	704	120	75[a]	0	70[a] (26)	Trace	
O-*n*-Bu	O-*n*-Bu	O-*n*-Bu	2.0	704	120	80[a]	0	75[a] (40)	Trace	
O-*i*-Pr	O-*i*-Pr	O-*i*-Pr	2.0	301	120	80[c]	85[c] (63)	4[c]	10	
O-*sec*-Bu	O-*sec*-Bu	O-*sec*-Bu	2.0	928	120	80[c]	85[c] (59)	3[c]	12	
OMe	OMe	OC_6H_5	2.0	672	120	20	65[b,d]	0	0	10[e] 10[f]
OMe	$-OCH_2CH_2O-$		1.4	4[g]	110	60[c]	0	100[c,d] (45)	Trace	
Me	OMe	OMe	1.0	16	80	100	100[h]	0	0	

[a] Yield calculated by vpc method A (isolated yield in parenthesis). Based on reacted dione. [b] Observed products were a result of thermal Arbuzov rearrangements of precursors. [c] Vpc method B. [d] Methyl carboxylate, 10 hr. [e] Methyl 2,2,4-trimethyl-3-oxovalerate. [f] Phenyl 2,2,4-trimethyl-3-oxovalerate. [g] Months. [h] From weight of crude product shown by nmr to be nearly pure.

general structures **8** and **9**. The relative amounts of these adducts were found to be dependent on the group R as shown in Table I.



8

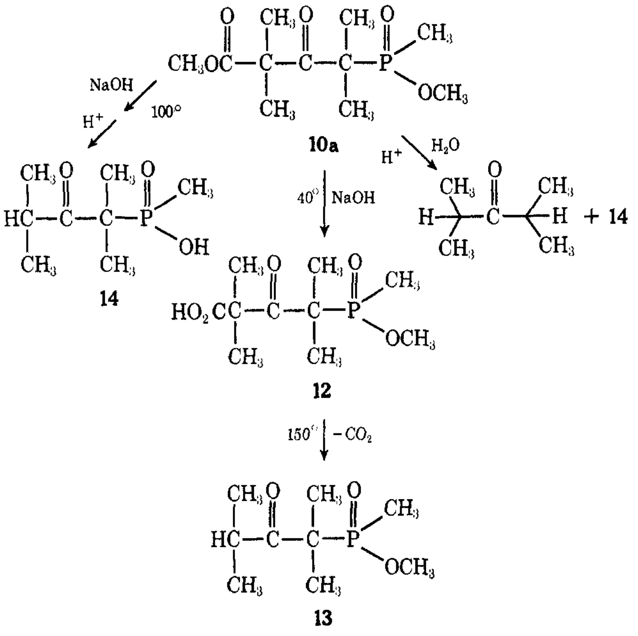


9

The structure of **8a**, R = CH_3, was proved rigorously by chemical as well as spectroscopic means. Products **8** from other phosphites were identified by spectral comparisons and quantitative elemental analysis. All were shown (Table II) to exhibit pmr resonances (singlet) of appropriate area assignable to the isolated *gem*-methyls (CH_{3A}) in the range δ 1.29–1.49, and a 6 H doublet (J_{HP} = 11 Hz) at δ 1.17–1.49 resulting from the *gem*-methyl grouping adjacent to phosphorus (CH_{3B}). Ready conversion with methyl iodide at room temperature to the corresponding methylphosphinate **10** or on warming with elemental sulfur to the thiophosphonate **11** showed products **8** to be trivalent. Apparently a combination of hindered rotation and/or the asymmetry of phosphorus[10] in the methylphosphinate rendered the methyls of each geminal pair nonequivalent. The isolated pair (CH_{3A}) now appears as two singlets at δ 1.38–1.50 and the CH_{3B} protons as two doublets at δ 1.42–1.58. The only exception is **10h** with a single peak at δ 1.49 for the isolated *gem*-methyl pair and pair of *gem*-methyls on the carbon α to phosphorus with coincidentally identical chemical shifts (δ 1.62). Their nonequivalence is shown by the fact that they have different J_{HP} values as do those of the other compounds (**10**). It is interesting that the effect is often greater on the more remote A protons than on the adjacent B protons in a given molecule. The unusually high chemical shifts for the A and B methyl protons of **10h** probably result from shielding by the aromatic ring.

Chemical degradation provides convincing evidence for the structure of **10a**. In Scheme I are given the reactions employed along with the products formed. (See Experimental Section for complete spectral, physical, and analytical data on **12**–**14**.) Mild treatment with aqueous NaOH led largely to saponification of the carboxy ester group to give **12** as noted chiefly by loss of the methoxy singlet in the pmr and introduction of unmistakeable CO_2H ir absorption. [The low-frequency carbonyl absorption in all these compounds is assigned to the highly hindered ketone grouping which is situated in a position similar to that of the carbonyl in di-*tert*-butyl ketone[11] (1687 cm^{-1}).] Vigorous saponification conditions (100°) cleaved both the carboxylate and phosphinate esters to give the phosphinic acid **14**. This compound clearly shows the presence of an isopropyl group in the pmr and loss of the methoxyl doublet ($POCH_3$). The doublet as-

SCHEME I



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(10) Long-range effects of asymmetric phosphorus centers are well established: L. Frankel, J. Cargioli, H. Klapper, and R. Danielson, *Can. J. Chem.*, **47**, 3167 (1969); R. V. Jardine, A. H. Gray, and J. B. Reesor, *ibid.*, **47**, 35 (1969); L. S. Frankel, H. Klapper, and J. Cargoli, *J. Phys. Chem.*, **73**, 91 (1969); D. G. Rowsell, *J. Mol. Spectrosc.*, **23**, 32 (1967); R. Keat, W. Sim, and D. S. Payne, *Chem. Commun.*, 191 (1968); W. McFarlane, *ibid.*, 229 (1968); A. P. Lane, D. A. Morton-Blake, and D. S. Payne, *J. Chem. Soc. A*, 1492 (1967); T. H. Sidall, III, *J. Phys. Chem.*, **70**, 2249 (1966); T. H. Sidall, III, and C. A. Prohaska, *Inorg. Chem.*, **4**, 783 (1965); *J. Amer. Chem. Soc.*, **84**, 2502, 3467 (1962).

(11) J. Lascombe, P. Grange, and M. Josien, *Bull. Soc. Chim. Fr.*, 773 (1957).

signed to the *gem*-methyl grouping adjacent to phosphorus and the PCH_3 doublet, which are seen in the spectra of **8a**, **10a**, **12**, and **13**, persist. A single carbonyl absorption is now present (1696 cm^{-1}). Loss of one carbonyl absorption and the introduction of an isopropyl group (pmr) also accompanies the decarboxylation of **12** at 150° to **13**. The pmr spectrum of **13** is identical with that of **14** except for the presence of the $POCH_3$ doublet in the **13** spectrum and small chemical shift differences. The single sharp peak in the ir at 1225 cm^{-1} is clearly that of the phosphinate phosphoryl bond.[12] The mass spectrum of **13** also confirmed its structure. Elemental analyses were obtained for **12** and **14**.

Acid hydrolysis of **10a** gives both decarboxylation and carbon–phosphorus cleavage. The latter finds precedent in other hydrolyses of compounds which have a phosphoryl group β to a ketone carbonyl.[13] The isopropyl ketone formed firmly established the carbon skeleton of **10a**.

With tri-*n*-propyl, tri-*n*-butyl, and methyl ethylene phosphites, no products of type **8** or **10** were detected. The proportions of **8** and **9** from the trimethyl and triethyl phosphite reactions were dependent on the extent of reaction. This is shown clearly for the triethyl phosphite reaction in Table III. The ratio **9**/**8** increased with time. Table IV presents evidence using triethyl phosphite that **8** is actually formed reversibly. That is, a mixture of **8b** and **9b** containing no phosphite or dione when allowed to stand at room temperature or heated to 120–150° is observed to give dione, phosphite, and a trace of lactone **4** along with a slow decrease in **8b** and proportionate increase in **9b**. **9b** heated alone does not give **3**, **4**, or **8b**.

In every reaction of phosphite with dione a small amount of lactone (<5%) was formed and persisted throughout the reaction with the exception of the reaction of dimethyl phenyl phosphite, which also gives no lactone product **9**. A relatively large amount of lactone **4** built up during reaction of the secondary alkyl phosphites.

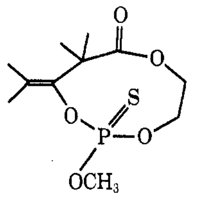
Dimethyl methylphosphonite proved to be very reactive with dione, the reaction being complete at 80° in 18 hr. The product **8i** underwent isomerization to the dimethyl phosphinate at room temperature in a few days. At 120° isomerization was complete in a maximum of 3 hr. No evidence was found for formation of either the starting phosphonite, dione, lactone, or **9i** under isomerization conditions.

When the dione **3** was heated with tri-*n*-butylphosphine at 120° for 18 hr, it was completely consumed and converted to the lactone and its polymer 22. The polymer is identical with that formed from reaction of **4** with traces of sodium methoxide.[14]

Lactone Reactions.—When **4** was heated with the above phosphites and dimethyl methylphosphonite, products of the general type **9** were formed exclusively. No **8** has ever been observed in any reaction of these or any other trivalent phosphorus derivatives with **4**. The products and yields are listed in Table V. Physical and spectral data for **9** and sulfur derivatives (**15**) or methyl iodide Arbuzov products **16** appear in Table VI. Characteristic of the ir spectra in each case, **9**, **15**, and **16**, was an intense band at 1730 cm^{-1} (C═O) and a weak absorption near 1670 cm^{-1} (C═C). The nmr spectra peaks assignable to the vinyl methyls are at δ 1.47–1.55 (J_{PH} = 3.0–5.0) and 1.67–1.73 (J_{HP} = 1.5–3.5). **16h** and **16h′** fall somewhat outside the chemical shift range as a result of the shielding effects of the phenoxy groups. Griffin and Gordon have assigned the larger couplings in $H_3CC{=}CCP$ systems to the methyl group trans to phosphorus.[15] Products **9**, **15**, and **16** ($CDCl_3$) showed a single peak for the *gem*-methyls at δ 1.30–1.34 for the phosphites **9** and 1.41–1.43 for **15** and **16** with the exception of **16h** and **16h′**, again affected by the phenyl. The asymmetric center at phosphorus in **16h** and **16h′** apparently does not affect the CH_{3C} pair which appears as a singlet.

Chemical evidence for the structure **9a**, the adduct of **4** with trimethyl phosphite, arises from the facile acid- or base-catalyzed methanolysis of **9a** to trimethyl phosphite and methyl 2,2,4-trimethyl-3-oxovalerate and its acid-catalyzed hydrolysis to the same valerate. **9d** and **9g** were similarly converted to the corresponding ester and phosphite.

Several of the reactions with lactone deserve special mention. Methyl ethylene phosphite gives two products, one from migration of methoxy to carbonyl to give methyl carboxylate **9g** (isolated as **15g**). The structure of **9g** was further shown by its methanolysis products. A minor product of the reaction appeared to come from migration of ring oxygen to give a nine-membered ring product isolated as the thiophosphate **17-S**. Spectral and elemental analysis data (Experimental Section) were entirely consistent with structure **17-S**.



17-S

With dimethyl phenyl phosphite, lactone **4** gave both methyl and phenyl carboxylates isolated as the methylphosphonates, **16h** and **16h′**. In contrast this phosphite gave only methyl carboxylate with dione **3**. Because of extended reaction times the latter product had been isomerized to the methylphosphonate, **10h**.

Triisopropyl and tri-*sec*-butyl phosphites reacted with the lactone in an unusual manner. Both reactions proceeded very slowly compared to those of the *n*-alkyl counterparts, tri-*n*-propyl and tri-*n*-butyl. Further, very little 1:1 adduct **9** was formed (Table V). Only a small amount of somewhat impure **9e** and **9f** could be isolated, but these were readily characterized by their ir and nmr spectra. The sulfur derivatives **15e** and **15f** decomposed on attempted vpc purification. The major product in each instance consisted of polyenol ester material containing 2–3 lactone units for every

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[12] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958, p 312.

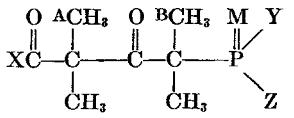
[13] N. Kreutzkamp and H. Kayser, *Chem. Ber.*, **89**, 1614 (1956); A. N. Pudovik and B. A. Arbuzov, *Dokl. Akad. Nauk SSSR*, **73**, 327 (1950); L. D. Freedman and G. O. Doak, *Chem. Rev.*, **57**, 479 (1957).

[14] R. H. Hasek, R. D. Clark, E. U. Elan, and J. C. Martin, *J. Org. Chem.*, **27**, 60 (1962).

[15] D. J. Martin, M. Gordon, and C. E. Griffin, *Tetrahedron*, **23**, 1831 (1967).

Table II

Physical, Spectral, and Analytical Data for[a]


$XC(=O)-C(^{A}CH_3)(CH_3)-C(=O)-C(^{B}CH_3)(CH_3)-P(=M)(Y)Z$

Compd[b]	X	Y	Z	M	Chemical shifts[c] (J_{HP} or J_{HH})[d]					Solvent	Ir bands, cm^{-1}	Bp or mp, °C
					CH_{3A}	CH_{3B}	X[e]	Y[e]	Z			
10a	CH_3O	CH_3O	CH_3	O	1.39 (s) 1.48 (s)	1.39 (d, 15.0) 1.41 (d, 15.5)	3.29 (s)	3.32 (d, 10.5)	1.36 (d, 14.0)	Benzene	2990, 2953, 1743, 1720 (w), 1687, 1465, 1395, 1372, 1305, 1265, 1230, 1195, 1145, 1050, 1035, 1005, 987, 892, 797, 745 (film)	95 (0.1 Torr)
8a	CH_3O	CH_3O	CH_3O		1.29 (s)	1.17 (d, 11)	3.67 (s)	3.58 (d, 10.5)	3.58 (d, 10.5)	CCl_4	2987, 2940, 2837, 1750, 1732 (w), 1687, 1472, 1394, 1372, 1270, 1200, 1065, 1042, 1008, 994, 907, 747 (film)	76–77 (0.03 Torr)
8b	C_2H_5O	C_2H_5O	C_2H_5O		1.30 (s)	1.23 (d, 11)	1.22, OCH_2CH_3 (t, 7) 3.9,[f] OCH_2CH_3 (m)	1.30, OCH_2CH_3 (t, 7) 3.9, OCH_2CH_3 (m)		CCl_4	2980, 1740, 1680, 1462, 1388, 1267, 1148, 1103, 1063, 1040, 1000, 920, 740 (film)	106 (0.2 Torr)
10b	C_2H_5O	C_2H_5O	CH_3	O	1.38 (s) 1.42 (s)	1.43 (d, 15) 1.43 (d, 16)	0.91, OCH_2CH_3 (t, 7) 3.8,[f] OCH_2CH_3 (m)	0.98, OCH_2CH_3 (t, 7) 3.8,[f] OCH_2CH_3 (m)	1.37, PCH_3 (d, 14)	Benzene	2980, 1745, 1695, 1473, 1390, 1370, 1300, 1255, 1220, 1162, 1142, 1030, 957, 884, 787 (film)	
8e	i-C_3H_7O	i-C_3H_7O	i-C_3H_7O		1.33 (s)	1.27 (d, 11.5)	1.19, $HC(CH_3)_2$ (d, 6) 5.0, $OCH(CH_3)_2$ (m)	1.23, $HC(CH_3)_2$ (d, 6) 4.2, $OCH(CH_3)_2$ (m)	1.25, $HC(CH_3)_2$ (d, 6)	$CDCl_3$	2980, 1730, 1670, 1465, 1385, 1258, 1148, 1108, 1030, 980, 952, 899, 862, 754, 742 (film)	62–72 (0.025 Torr)
11e	i-C_3H_7O	i-C_3H_7O	i-C_3H_7O	S	1.49 (s)	1.62 (d, 19.5)	1.06, $HC(CH_3)_2$ (d, 7) 4.8,[f] $HC(CH_3)_2$ (broad m)	1.18, $HC(CH_3)_3$ (d, 7) 4.8, $HC(CH_3)_2$ (broad m)	1.27, $HC(CH_3)_2$ (d, 7) 4.8, $HC(CH_3)_2$ (broad m)	Benzene	2980, 1735, 1720 (w), 1690, 1465, 1385, 1255, 1165, 1146, 1106, 900, 888, 784 (film)	
10e	i-C_3H_7O	i-C_3H_7O	CH_3	O	1.43 (s) 1.50 (s)	1.50 (d, 15) 1.52 (d, 15.5)	1.03, $HC(CH_3)_2$ (d, 7) 4.5,[f] $HC(CH_3)_2$ (m)	1.03, $HC(CH_3)_2$ (d, 7) 4.5, $HC(CH_3)_2$ (m)	1.43 (d, 14)	Benzene	2980, 1730, 1715 (w), 1680, 1465, 1383, 1255, 1220, 1166, 1148, 1108, 983, 897, 775 (film)	
8f	sec-C_4H_9O	sec-C_4H_9O	sec-C_4H_9O		1.49 (s)	1.47 (d, 11)	1.07, $OCH(CH_3)C_2H_5$ (d, 7) 4.8, $OCH(CH_3)C_2H_5$ (m)	1.10, 1.13 $OCH(CH_3)C_2H_5$ (d, 7) 3.8, $OCH(CH_3)C_2H_5$ (m) 0.86,[f] $OCH(CH_3)CH_2CH_3$ (broad overlapping t, ~7) 1.5,[f] $OCH(CH_3)CH_2CH_3$ (broad m)		Benzene	2980, 2950, 1735, 1680, 1465, 1385, 1258, 1150, 1125, 1115, 1098, 1029, 995, 926, 838, 793, 730 (film)	116–117 (0.25 Torr)

10f	*sec*-C_4H_9O	*sec*-C_4H_9O	CH_3	O	1.40 (s)	1.48 (d, 14.0)	0.79, 0.86	$OCH(CH_3)CH_2CH_3$ (broad, t)	1.38 (13.5)	Benzene	2980, 1730, 1720 (w), 1685, 1465, 1385, 1297, 1250, 1222, 1162, 1150, 1112, 1092, 1030, 992, 955, 874 (film)
					1.43 (s)	1.52 (d, 14.5)	1.10[f]	$OCH(CH_3)CH_2CH_3$ (d, 7)			
							1.5[f]	$OCH(CH_3)CH_2CH_3$ (broad m)			
							4.3, 4.8	$OCH(CH_3)CH_2CH_3$ (multiplets)			
10h	CH_3O	C_6H_5O	CH_3	O	1.49 (s)	1.62 (d, 15)	3.78 (s)	7.3 (m)	1.69 (d, 14)	$CDCl_3$	2950, 1730, 1690, 1590, 1495, 1385, 1365, 1250, 1200, 1150, 1070, 1030, 1000, 813, 793, 685, 638 ($CHCl_3$)
						1.62 (d, 16)					
10i	OCH_3	CH_3	CH_3	O	1.36 (s)	1.30 (d, 14.0)	3.24 (s)	1.21 (d, 12.0)	1.21 (d, 12.0)	Benzene	2980, 1750, 1730 (w), 1695, 1480, 1397, 1387, 1320, 1305, 1275, 1165, 1050, 1013, 1000, 949, 830, 880, 673 ($CHCl_3$)

[a] All compounds are colorless liquids or oils, unless otherwise noted. [b] Satisfactory C, H, and P analyses (±0.4%) were obtained for each of these compounds with the following exceptions. **10b**, an Arbuzov reaction product, was analyzed as the parent compound **8b**. **8e** was analyzed as its sulfur derivative **11e**. The Arbuzov product **10e** was not analyzed. **8f** was analyzed as its Arbuzov product **10f**. [c] In ppm downfield from internal TMS. [d] Multiplicity and coupling constant (J_{HP} or J_{HH}) in parenthesis below chemical shift value. [e] In some instances it was not possible to make a clear choice of assignment of chemical shifts when the same type of group was attached to both carbonyl and to phosphorus. Arbitrary assignments are made. [f] Resolution would not allow distinction between phosphorus and carbon attachment of the group.

TABLE III

EFFECT OF TIME AND SOLVENT ON **9**/**8** RATIO FROM REACTION OF DIONE **3** WITH TRIETHYL PHOSPHITE, 150°

Solvent	Time, hr[a]	% unreacted **3**[b]	**9**/**8**[c]
None	68	39	1.2
None	143	33	2.7
None	398	21	9.0
CH_3CN	144	49	2.7
CH_3CN	305	42	3.2
CH_3CN	660	34	7.4
n-C_7H_{16}	144	55	0.67
n-C_7H_{16}	305	60	0.72
n-C_7H_{16}	660	48	2.1

[a] Trace (<5%) of **4** noted at all times after start of reaction. [b] Determined from vpc by reference to internal standard decane. [c] Ratio of peak areas by vpc.

TABLE IV

CONVERSION OF **8b** TO **9b**

T, °C	Time, hr	Amount of product[a]				
		$(C_2H_5O)_3P$	**3**[b]	**8b**	**9b**	**9b**/**8b**[c]
25	0					0.50
25	168					0.65
25	336					0.65
120	27					1.1
120	160					2.0
150	0	0.63[d]	<0.1	2.6	1.7	0.65
150	24	1.9	0.85	0.40	1.8	4.5
150	87	1.5	0.80	0.17	2.1	13
150	111	1.6	0.52	0.18	2.5	14

[a] Figures reported are peak areas by vpc relative to that of internal standard decane. Total area 4.2 ± 0.5. Trace (relative area <0.07) of **4** noted in all samples except at $t = 0$. [b] Based on soluble **3** only. Considerable amounts crystallized out of reaction mixture before analysis. [c] Ratio peak areas by vpc. [d] A sample which originally contained **9b**/**8b** ratio of 0.5 and no dione or phosphite which had been kept 1 week at room temperature.

phosphite unit. This was supported by the fact that several times as much **4** was consumed as was phosphite.

Attempted reactions of a four-membered ring monoketone, 2,2,4,4-tetramethylcyclobutanone, with trimethyl phosphite and with trisdimethylaminophosphine failed to show any vpc evidence of reaction in 3 weeks at 115°. However, the phosphine and 3-dicyanomethylene-2,2,4,4-tetramethylcyclobutanone were both consumed at 60° in 3 weeks as were the above cyano ketone and trimethyl phosphite after 15 days at 120°. No vpc evidence for formation of tractable product was found.

Discussion

Most aspects of our results can be explained reasonably in terms of Scheme II by consideration of the effects of structure on the relative rates of various steps and stabilities of the proposed intermediates and products. The most remarkable aspect of these reactions is the failure in many instances to observe the same reaction pattern as was noted with other nucleophiles,[8] *i.e.*, formation of the same ring-opened product from either **3** or **4**. *E.g.*, alcohols give alkyl 2,2,4-trimethyl methyl-3-oxobutyrate on reaction with either **3** or **4**. We interpret the phosphite results to mean that the likely formed initial adducts **5** and **6** do not in such cases undergo transformation to a common intermediate such as **7**. Plausible reactions which would account for failure to form common products are

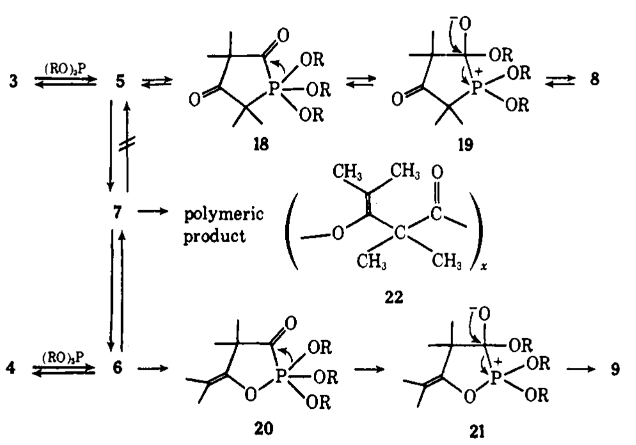
TABLE V

REACTIONS OF LACTONE **4** WITH PHOSPHITES AND PHOSPHONITE

PXYZ			Mol of PXYZ/ mol of **4**	Time, hr	*T*, °C	% convn[a]	% yield of **9**[a]	% yield of other products
X	Y	Z						
OMe	OMe	OMe	2.0	41	120	100	100[b] (74)	
OEt	OEt	OEt	2.0	81	120	95	100[b] (66)	
O-*n*-Pr	O-*n*-Pr	O-*n*-Pr	2.0	109	120	95	90[b] (48)	
O-*n*-Bu	O-*n*-Bu	O-*n*-Bu	2.0	109	120	95	95[b] (50)	
O-*i*-Pr	O-*i*-Pr	O-*i*-Pr	2.0	943	120	84	(15)[a]	high[a,c]
						22[d]	(28)[d]	
O-*sec*-Bu	O-*sec*-Bu	O-*sec*-Bu	2.0	928	120	45	(11)[a]	high[a,c]
						7[d]	(32)[d]	
OMe	OMe	OC_6H_5	2.0	408	120	80	40[e,f]	2[g]
							35[e,h] (35)[i]	15[j]
OMe	$-OCH_2CH_2O-$		2.0	369	110	65	15[e,k]	
							80[e,f] (61)[e,i]	

[a] Based on reacted lactone. [b] Yield calculated by vpc method A, isolated yields in parentheses. [c] Viscous cloud residue. [d] Based on reacted phosphite. [e] Vpc method B. [f] Methyl carboxylate. [g] Methyl 2,2,4-trimethyl-3-oxovalerate. [h] Phenyl carboxylate, Arbuzov rearranged. [i] Yield of mixture of products obtained by distillation. [j] Phenyl 2,2,4-trimethyl-3-oxovalerate. [k] Product is nine-membered ring containing a trialkyl phosphite and a carboxylic ester **17**.

SCHEME II



shown in Scheme II. In reaction **5** → **18** and **6** → **20** the incipient phosphonium enolate is trapped *via* a ring expansion to give a pentacovalent species, **18** or **20**. In this way the basic structure of **3** or **4** is preserved in the products **8** and **9**. Such a ring expansion is not unlike that noted in certain carbonium ion rearrangements.[16] Migration to a positive phosphorus center, however, is not a common reaction. This amounts to formation of a pentacovalent intermediate *via* intramolecular nucleophilic attack. The lack of reaction of 2,2,4,4-tetramethylcyclobutanone and the high reactivity of 3-dicyanomethylene-2,2,4,4-tetramethylcyclobutanone is indicative of negative charge development at carbon during the ring opening. We also believe the steps **18** → **19** and **20** → **21** as postulated to be novel. This reaction system is further unusual in that the ordinary Arbuzov-like reactions generally noted[6,7] for trialkyl phosphites and reactive carbonyl compounds are not observed.

Formation of **8** is depicted in Scheme II as being reversible in keeping with the interconversion of **8b** to **9b** (Table IV). Since the production of **3** and the phosphite accompanies **8b** → **9b**, the process **3** → **5** also is written as a reversible reaction.

The small steady state concentration of **4** formed during the reaction **8** → **9** and in all reactions of **3** which give some **9** is accommodated in Scheme II by ring opening to **7** followed by closure and reversal of the reaction converting **4** to **6**. In most cases the reaction of **4** is fast so that **4** does not build up to any extent. However, with the triisopropyl and tri-*sec*-butyl phosphites, **4** reacts only slowly thus allowing **4** to build up to account for 10–12% of dione consumed. The slow reaction of **4** with the branched alkyl phosphites may result, for reasons proposed below, from a greater degree of reversibility of **4** → **6** step. The sequence **3** → **5** → **7** → **6** → **4** also accounts nicely for the conversion of **3** to **4** by tributylphosphine. Since product formation cannot proceed through alkyl migration through intermediates **19** or **21**, **4** is formed. This interconversion may also be catalyzed by $AlCl_3$.[14] Apparently **4** is the thermodynamically more stable dimer of dimethylketene. The step **5** → **7** seems to be nonreversible as in no instance have we noted either production of dione or formation of **8** from reaction of lactone with any of 15–20 trivalent phosphorus nucleophiles.

Scheme II also accounts for the formation of both products **8** and **9** from reactions with **3**. Several influences likely will be important in determining the partition of products of reaction with **3** between products **8** and **9**. One is the relative rates of the reaction **5** → **18** and **5** → **7**. These will in turn be affected by the relative stabilities of **18** and **7**. **7** will be favored by substituents on phosphorus which stabilize a positive charge. Conversely, **18** will be stabilized by electron-withdrawing substituents.[17,18] Bulky substituents on phosphorus in **18** will probably destabilize **18**, since the trigonal bipyramidal structures of related pentacovalent species show considerable crowding about phosphorus.[19] To the extent that the process **5** → **18** is rapidly reversible, then the ease of the migration (step **18** → **19**) also will influence the distribution between **8** and **9**. The crossover between the routes to give **8** and **9** *via* **7** may indeed involve **18** and **20** rather than **5** and **6** in which case the ease of migration becomes an obvious factor in the choice between **8** and **9** formation from **3**. A

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[16] For examples in deamination reactions, see P. A. S. Smith, *Org. React.*, **11**, 1157 (1960).

[17] D. B. Denny and D. H. Jones, *J. Amer. Chem. Soc.*, **91**, 5821 (1969);

[18] F. Ramirez, C. P. Smith, J. F. Pilot, and A. S. Gulati, *J. Org. Chem.*, **33**, 3787 (1968); F. Ramirez, J. F. Pilot, O. P. Madan, and C. P. Smith, *J. Amer. Chem. Soc.*, **90**, 1275 (1968).

[19] W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *ibid.*, **89**, 2268 (1967); R. D. Spratley, W. C. Hamilton, and J. Ladell, *ibid.*, **89**, 2272 (1967).

second important consideration, where the question of relative amounts of **8** and **9** is concerned, is the previously discussed conversion of **8** to **9**. This phenomenon readily explains the observed (Table III) time dependence of **8**/**9** ratio for both the trimethyl and triethyl phosphite reactions. It may be important in cases where no **8** is formed. Thirdly, we would suggest that the ease of subsequent irreversible thermal Arbuzov rearrangement of **8** to **10** also can be an important factor in the **8**/**9** ratio, since the conversion of **8** → **9** can be thereby prevented. *E.g.*, we have found that **8a** undergoes considerable rearrangement to **10a** at 150°. This is not true of **8b**. In a reaction at 150° of dione and trimethyl phosphite in heptane, 40% of the dione was consumed in 200 hr at which time the ratio of (**8a** + **10a**)/**9a** was 85/15, and the **10a**/**8a** ratio was about 5/95. After about 500 hr the **8a**/**9a** ratio was only reduced to 50/50. In the meantime the **10a**/**8a** ratio was increased to 67/33. By contrast, as noted in Table III, at about 45% reaction at 150° of **3** and $(C_2H_5O)_3P$, the **8b**/**9b** ratio is 68/42. After another several hundred hours the ratio is reduced to 33/67. In another experiment in a neat reaction of **3** with triethyl phosphite, after extensive heating only 5% of **8b** remained. The reaction with triethyl phosphite allows more of the **8b** to be converted to **9b** since **8b** is not isomerized to **10b**. At 120° less **8a** than **10a** occurs, but the **8a**/**9a** ratio at 25 and 50% conversions of **3** only changed from 97/3 to 83/13. Thus, the propensity toward reversal of **8a** formation also is reduced at the lower temperature.

We suggest that the failure to observe formation of **8** in the reactions of the longer chain phosphites, tri-*n*-propyl and tri-*n*-butyl, may result from the following. In these cases product **8**, if formed, probably would not undergo the **8** → **10** isomerization, and any **8** formed initially may be rapidly isomerized to **9**. Alternately, since no **8** is ever detected at any stage in these reactions, the increased alkyl chain lengths in the alkoxy groups attached to phosphorus may have induced steric strain in the phosphorane **18**. Consequently, the rate of formation of **18** may be significantly decreased leading to predominant conversion of **5** to **7**.

In the reaction of phenyl dimethyl phosphite with dione, no product **9** is seen, and not even traces of lactone **4** are noted. The rate of reaction of this phosphite with both **3** and **4** is reduced by the phenoxy substituent, and it seems likely that phosphorus in **8** would also be of reduced nucleophilicity which precludes the conversion of **8** to **9** in this instance. Another factor could be reduced stability of **7** resulting from replacement of CH_3O by C_6H_5O.

Reaction of **3** with methyl ethylene phosphite gives no **8**. Such a result is not unreasonable, since the presence of two five-membered rings might be expected to force the methoxy into predominantly the equatorial position where it would be less reactive.[20] The rate of the step **18** → **19** would then be reduced for the adduct **18** from methyl ethylene phosphite allowing an increased proportion of reaction to proceed through **7**. Apparently the expected increased stability of **18** from the presence of a second five-membered ring is not able to direct the reaction in favor of **8**. This again suggests that the migration step may be of controlling importance. It may be noted that the product of methoxyl migration is still observed. This suggests that placement of an alkoxy group in a five-membered ring lowers its migration potential in spite of the preferred axial position of the ring oxygen.

The **8** → **9** product distribution from reaction of **3** with dimethyl methylphosphonite is not strictly comparable to the others since the reaction temperature is low. Formation of **8i** at 80° is not reversible; and at higher temperatures **8i** is readily converted to **10i** which may preclude formation of **9i**.

We find the results of the dione reactions with triisopropyl and tri-*sec*-butyl phosphite difficult to rationalize. Factors which would destabilize **18** in the tri-*n*-propyl and tri-*n*-butyl cases would be expected to be operative here as well. For some unknown reason, alkoxy migration may be rapid and may, in fact, relieve strain in **18**. Alternatively; the branched alkyl cases may simply undergo reversal of **8** formation very slowly compared to the *n*-alkyl cases because of steric hindrance.

The lactone reactions seem fairly straightforward with the exception of triisopropyl and tri-*sec*-butyl phosphites. The low reactivity of **3** and the building up of **4** in the analogous reactions of **3** with these nucleophiles suggests that the **4**–**6** conversion is highly reversible. Steric strain in the intermediate **6** may be an important factor. The predominance of product containing several lactone molecules for every phosphite suggests that **7** is favored kinetically or thermodynamically over **20** or its subsequent products. **7** apparently adds more molecules of lactone before the ultimate product is formed.

When only alkyl substituents are attached to phosphorus, as in tri-*n*-butylphosphine, **7** adds to several molecules of **4** before the phosphine is removed giving the polymer **22**.

Finally, the greater ease of methoxy over phenoxy migration in the dione reaction and their nearly equal migrational abilities in the lactone reaction are of considerable interest but are not readily explainable. Migrational aptitudes could depend on several kinetic factors: product stability; stability of the leaving alkoxide; stability of the charge on phosphorus; and position, axial or equatorial, of the potential leaving group. The dimethylphenyl phosphite reactions with **3** and **4** appear to be somewhat anomalous in that the phenyl and methyl 2,2,4-trimethyl-3-oxobutyrates are formed in a manner unknown. In all other cases the indication is that migration is strictly intramolecular, since external alkoxide would readily polymerize the lactone. The question of migrational abilities will be explored more fully in the following paper.

Experimental Section

Materials and Methods.—Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and at the Celanese Chemical Co., Technical Center.

Infrared spectra were obtained on Beckman IR-5A and Perkin-Elmer 421 spectrophotometers. Unless otherwise noted, reported ir bands are of strong or medium strength. Proton mag-

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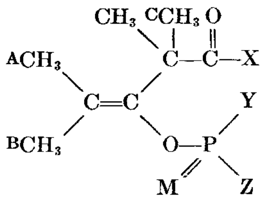
[20] The influences of ring size and electronegativity on axial and equatorial preferences of substituents on pentacovalent phosphorus as well as the relative reactivities of axial and equatorial positions have been summarized recently: E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970); F. H. Westheimer, *ibid.*, **1**, 70 (1968); K. Mislow, *ibid.*, **3**, 321 (1970); F. Ramirez, *ibid.*, **1**, 168 (1968).

TABLE VI

PHYSICAL, SPECTRAL, AND ANALYTICAL DATA FOR[a]



Compd[b]	X	Y	Z	M	Chemical shifts[c] (J_{HP} or J_{HH})[d]					Solvent	Ir bands, cm^{-1}	Bp or mp, °C
					CH_{3A}	CH_{3B}	CH_{3C}	X[e]	Y, Z[e]			
9a	CH_3O	CH_3O	CH_3O		1.47 (d, 3.0)	1.67 (d, 1.5)	1.34 (s)	3.65 (s)	3.75 (d, 10)	Neat	2982, 2945, 1732, 1665 (w), 1457, 1392, 1280, 1260, 1195, 1150, 1123, 1080, 1035, 1022, 817, 750 (film)	64–66 (0.06 Torr)
9b	C_2H_5O	C_2H_5O	C_2H_5O		1.48 (d, 3.0)	1.70 (d, 1.5)	1.30 (s)	1.18, OCH_2CH_3 (t, 7) 4.0, OCH_2CH_3 (m)	1.23, OCH_2CH_3 (t, 7) 4.0, OCH_2CH_3 (m)	Neat	3000, 2950, 1730, 1670 (w), 1470, 1390, 1255, 1150, 1123, 1050, 945, 925, 812, 750 (film)	72–74 (0.1 Torr)
9c	n-C_3H_7O	n-C_3H_7O	n-C_3H_7O		1.48 (d, 3.0)	1.68 (d, 1.5)	1.30 (s)	0.95,[e] $OCH_2CH_2CH_3$ (m) 1.5, $OCH_2CH_2CH_3$ (m) 3.9, OCH_2CH_3 (m)		Neat	2960, 2900, 1730, 1675 (w), 1470, 1390, 1255, 1150, 1063, 1018, 980, 868, 809 (film)	100–103 (0.08 Torr)
15c	n-C_3H_7O	n-C_3H_7O	n-C_3H_7O	S	1.52 (d, 4.0)	1.74 (d, 3.0)	1.43 (s)	1.0,[e] $OCH_2CH_2CH_3$ (broad t, 7) 1.5, $OCH_2CH_2CH_3$ (m) 4.0, $OCH_2CH_2CH_3$ (m)		$CDCl_3$	2980, 1730, 1670 (w), 1465, 1380, 1245, 1143, 1055, 1000, 966, 900, 866, 758 (film)	
9d	n-C_4H_9O	n-C_4H_9O	n-C_4H_9O		1.48 (d, 3.0)	1.69 (d, 1.5)	1.32 (s)	0.9,[e] $OCH_2CH_2CH_2CH_3$ (broad t, 7) 1.1–1.9, $OCH_2CH_2CH_2CH_3$ (broad multiplet) 3.9, $OCH_2CH_2CH_2CH_3$ (broad m)		Neat	2950, 1730, 1670 (w), 1465, 1385, 1250, 1150, 1065, 1028, 968, 812, 775 (film)	115–118 (0.08 Torr)
15d	n-C_4H_9O	n-C_4H_9O	n-C_4H_9O	S	1.51 (d, 4.0)	1.72 (d, 3.0)	1.42 (s)	1.0,[e] $OCH_2CH_2CH_2CH_3$ (broad t, 7) 1.1–1.9 $OCH_2CH_2CH_2CH_3$ (broad m) 4.0, $OCH_2CH_2CH_2CH_3$ (m)		$CDCl_3$	2960, 1730, 1670 (w), 1465, 1380, 1248, 1145, 1115, 1055, 1025, 985, 898, 865, 807, 735 (film)	

15g	CH_3O	OCH_2–CH_2O		(S)	1.55 (d, 5.0)	1.73 (d, 3.5)	1.41 (s)	3.69, OCH_3 (s)	4.45, OCH_2CH_2O (m)	$CDCl_3$	2980, 2930, 1730, 1630 (w), 1465, 1385, 1250, 1190, 1150, 1110, 1075, 1030, 960, 925, 862, 814, 735, 690 (film)	84–85 (white solid)
16h	C_6H_5O	CH_3O	CH_3	O	1.65 (d, 4.0)	1.81 (d, 2.5)	1.58 (s)	7.2, C_6H_5O (m)	3.77, OCH_3 (d, 11.5) 1.58, PCH_3 (d, 18)	$CDCl_3$	2950, 1740, 1670 (w), 1590, 1490, 1315, 1250, 1198, 1165, 1118, 1074, 1042, 962, 933, 858, 813, 685, 643 (film)	
16h′	CH_3O	C_6H_5O	CH_3	O	1.55 (d, 4.0)	1.81 (d, 2.5)	1.50 (s)	3.74, OCH_3 (s)	7.3, OC_6H_5 (m) 1.75, PCH_3 (d, 18)	$CDCl_3$	2950, 1730, 1670 (w), 1590, 1495, 1425, 1250, 1215, 1150, 1110, 1075, 962, 938, 858, 687, 645 (film)	
16i′	OCH_3	CH_3	CH_3	O	1.42 (3.0)	1.52 (2.5)	1.65 (s)	3.38 (s)	1.17 (d, 14.0)	Benzene	2978, 2919, 1730, 1670 (w), 1480, 1397 (w), 1377 (w), 1305, 1310, 1280, 1265, 1260, 1205, 1163, 1130, 1022, 955, 932, 872, 830, 778 (film)	

[a] All compounds are colorless liquids or oils, unless otherwise noted. [b] Satisfactory C, H, and P analyses (0.4%) were obtained for each of these compounds. **9d** was analyzed as its sulfur derivative **15d**. **16h** and **16h′** were analyzed as a mixture as were **15g** and **17-S**. [c] In ppm downfield from internal TMS. [d] Multiplicity and coupling constant (J_{PH} or J_{HH}) in parentheses below chemical shift value. [e] Resolution would not allow distinction between phosphorus and carbon attachment of certain groups because of a coincidental overlap of resonances.

netic resonance (pmr) spectra were obtained on Varian A-60 and A-56/60 instruments using tetramethylsilane (TMS) as internal standard. Reported chemical shifts are in δ, parts per million downfield from TMS. Multiplicity pf peaks is indicated by s, singlet; d, doublet; t, triplet; and m, multiplet. To resolve spectra complicated by overlapping peaks a technique was used which involved addition of incremental amounts of benzene to a $CDCl_3$ solution of the compound being analyzed. By observing the change in positions of peaks after each benzene addition, it was possible to sort out chemical shifts and coupling constants. Mass spectral data were taken on Consolidated Electrodynamics Corp. Type 21-110 and Perkin-Elmer Model 270 instruments.

Vpc analyses were run on an F & M Model 810 instrument and also on an Aerograph Model A90-P3 chromatograph, both thermal conductivity units. Analytical work was done on either column A, a 6 ft by 0.25 in. 20% SE-30 on 60–80 mesh Chromosorb W, or column B, a 6 ft by 0.25 in. 30% Celanese Ester No. 9 on the same solid support, both at 120 ml/min flow rate. Preparative vpc was accomplished with a 10 ft by $^3/_8$ in. 20% SE-30 on Chromosorb W column at 200 ml/min flow rate. Two analytical methods were used. **Method A.** A weighed amount of toluene or tetralin was introduced as internal standard following the reaction. The relative areas of standard and each component were measured by triangulation or planimetry. In several cases relative sensitivities were measured and shown not to vary by more than 10%. This is probably also a measure of overall accuracy of the measurement and in the relative yields are of most interest was deemed adequate for the purposes of the experiments. **Method B.** Under identical chromatographic conditions and injection sample sizes, the total area of reactants was determined before reaction and that of remaining reactants and of products formed after reaction. Percentage yields of products were calculated on the basis of starting materials consumed using the measured areas and assumed equal sensitivity of all peaks.

All reactants were reagent commercial materials, often distilled before use, or were prepared by standard reference procedures except for the following. Commerical phosphite samples were distilled from sodium before use. **2,2,4,4-Tetramethylcyclobutanone** was prepared from the dione using the procedure of Shechter.[21] 2,2,4,4-Tetramethyl-1,3-cyclobutanedione (100 g, 0.715 mol) was dissolved in 95% ethanol. Water was added until the solution turned turbid, and then ethanol was added until turbidity disappeared. Semicarbazide hydrochloride (200 g, 1.79 mol) and sodium acetate (200 g) were added to the solution which was then heated several hours on a steam bath. After sitting overnight at room temperature, the solid was removed by filtration and was washed several times with water. Drying under vacuum yielded the disemicarbazone, a white powder (197 g, 76% yield). Sodium (50.0 g, 2.17 mol) was dissolved slowly in ethylene glycol (500 ml). To the ethylene glycol solution in a three-necked 3-l. flask at 100° was added the disemicarbazone (65 g, 0.293 mol). Continued heating at 150° produced vigorous foaming. At 180° the foaming subsided and a pale yellow liquid distilled at 150°. The reaction mixture was maintained at 205° for 1.5 hr. After cooling, the solution was steam distilled. To the combined condensate from steam distillation and distillate collected during the heating process was added oxalic acid (150 g). The mixture was heated on a steam bath for several hours and then steam distilled. The condensate was extracted with three portions of chloroform. After being dried over calcium chloride, the solvent was removed using a rotary evaporator and an aspirator. Distillation yielded pure 2,2,4,4-tetramethylcyclobutanone, 10.2 g, 28% yield, bp 84–85° (158 Torr) [lit.[22] 77° (150 Torr)].

Methyl ethylene phosphite was prepared by heating a solution of trimethyl phosphite (125 g, 1.01 mol) and ethylene glycol (58.0 g, 0.935 mol), to which a small piece of sodium had been previously added, in a flask to which was connected a short column and distillation head. As the solution was heated and stirred, methanol distilled. When the evolution of methanol ceased, the solution was distilled from sodium through a Vigreux column to give methyl ethylene phosphite, 39.6 g, 0.325 mol, 35% yield, bp 62–65° (25 Torr). The pmr spectrum (benzene) corresponded to that given by Haake and coworkers.[23]

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(21) H. Shechter, private communication. We thank Professor Shechter for making the details of this preparation available to us.

(22) H. L. Herzog and E. R. Buchman, *J. Org. Chem.*, **16**, 99 (1951).

(23) P. Haake, J. P. McNeal, and E. J. Goldsmith, *J. Amer. Chem. Soc.*, **90**, 715 (1968).

Dimethyl Phenyl Phosphite.—Phosphorus trichloride (50.0 g, 0.364 mol) and triethylamine (37.1 g, 0.366 mol) were mixed with 500 ml of ether in an ice-cooled flask. With constant stirring phenol (34.3 g, 0.364 mol) in 200 ml of ether was added dropwise (addition required 3 hr). Triethylamine (73.8 g, 0.728 mol) was added rapidly followed by dropwise addition of methanol (23.4 g, 0.728 mol) in 250 ml of ether. The mixture was refluxed for 1 hr after which the amine hydrochloride was removed by filtration, and the solvent was removed under reduced pressure on a rotary evaporator. Distillation through a wire spiral column yielded pure dimethyl phenyl phosphite, 24.8 g, 0.133 mol. 37% yield, bp 62–63° (0.25 Torr) [lit.[24] 86° (12 Torr)]. The pmr spectrum (neat) showed a 6 H doublet at 3.55 ppm (J_{HP} = 10.5 Hz) and a 5 H multiplet at 7.2 ppm.

General Procedure for Reactions of Phosphites with Lactone (4).—All reactions were run neat under N_2 and monitored by vpc. Conditions are given in Table V along with yields determined. Products (**9**) were isolated by vacuum distillation. In most cases derivatives were prepared by gently warming the product with sulfur or by reaction at room temperature with methyl iodide. Such derivatives were purified by preparative vpc.

Physical and spectral data and analyses appear in Table V for routine reactions. More detailed discussions of unusual cases and of formation of derivatives appear below.

Trimethyl Phosphite.—Further evidence for the structure of product **9a** was provided by results of its hydrolysis and methanolysis. Treatment of **9a** with excess methanol containing a trace of *p*-toluenesulfonic acid gave only trimethyl phosphite and methyl 2,2,4-trimethyl-3-oxovalerate as shown by vpc as did methoxide-catalyzed room temperature methanolysis. Similarly, hydrolysis with dilute HCl in methanol–water gave only the valerate in 24 hr at room temperature.

Triethyl Phosphite.—Product **9b** (0.5 g) was allowed to stand at room temperature with an excess (1.5 ml) of methyl iodide for 2 days. Complete conversion (vpc method B) of **9b** to **16b**, a colorless viscous liquid, was observed. Vpc analysis showed only the isomerization product **16b** and a low-boiling product, presumably ethyl iodide. **16b** was not further purified: ir (film) 795, 848, 892, 926, 965, 1038, 1074, 1113, 1142, 1247, 1310, 1395, 1465, 1665 (w), 1720, 2930, and 2980 cm^{-1}; pmr (50/50 benzene–CDCl$_3$) δ 1.41 and 1.21 (6 H, t J_{HH} = 7 Hz, CH_3CH_2O), 1.41 (3 H, d, J_{HP} = 17 Hz, PCH_3), 1.46 (6 H, s, gem CH_3), 1.46 (3 H, d, J_{HP} = 4.0 Hz, vinyl CH_3), 1.72 (3 H, d, J_{HP} = 2.5 Hz, vinyl CH_3), 4.0 (4 H, m, OCH_2CH_3).

Tri-*n*-butyl Phosphite.—Because of the overlap of broad methylene absorptions in the nmr of **9d** with those for the geminal and vinyl methyl precluded accurate integration of the spectrum, the structure was further characterized by conversion of a 5% solution of **9d** in 1-butanol, to which had been added a trace of Na, at 100° in 3 days to high yields of tri-*n*-butyl phosphite and *n*-butyl 2,2,4-trimethyl-3-oxovalerate. Products were verified by retention time comparison with authentic samples on vpc columns A and B.

Triisopropyl Phosphite.—Lactone (5.00 g, 35.7 mmol) and triisopropyl phosphite (14.9 g, 71.6 mmol), heated at 120° for 943 hr, gave an 84% conversion of lactone and a 22% conversion of phosphite to products as shown by vpc monitoring. The lactone was consumed more rapidly than the phosphite indicating that something other than a 1/1 adduct was being formed. The amount of the products observed on vpc did not account for all of the lactone consumed. Distillation yielded 16% of the original lactone, 68% of the original phosphite, and a small amount of a colorless viscous liquid [15% yield based on reacted lactone and 28% based on reacted phosphite, bp 80–90° (0.15 Torr)]. This liquid was not isolated in sufficient quantity or purity to allow complete characterization. However, ir and pmr spectra of impure samples indicated that it was analogous to **9c** formed from tri-*n*-propyl phosphite and the lactone and thus was assigned the structure **9e**: pmr (benzene) δ 1.16 (18 H, d, J_{HH} = 7 Hz, $CH(CH_3)_2$), 1.46 (6 H, s, gem CH_3's), 1.53 (3 H, d, J_{HP} = 3.0 Hz, vinyl CH_3), 1.78 (3 H, d, J_{HP} = 1.5 Hz, vinyl CH_3), 4.6 (3 H, m, $OCH(CH_3)_2$); ir (film) 2980, 1730, 1670 (w), 1475, 1385, 1265, 1148, 1110, 1078, 1010, 865 cm^{-1}.

9e was converted by gentle warming with sulfur into the thiophosphate which decomposed upon attempted purification by vpc at 230° isothermal.

A large amount of undistillable, very viscous, cloudy residue remained from the distillation. The ir spectrum of the viscous residue (film) showed important absorptions at 760, 800, 862, 954, 982, 1060, 1110, 1250, 1385, 1465, 1670 (w), 1725, 1730, 2950, and 3000 cm^{-1}. Column chromatography failed to give pure samples of this residue, but pmr analysis of several fractions indicated a material containing 2–3 units of the lactone to 1 unit from the phosphite.

Tri-*sec*-butyl Phosphite 3 (5.00 g, 35.7 mmol) and the phosphite (17.8 g, 71.2 mmol) were heated at 120°. Heating for 928 hr yielded a 45% conversion of lactone to product but only a 7% conversion of phosphite to product (determined by vpc method C and distillation of reaction solution to recover starting materials). Distillation yielded a colorless viscous liquid **9f** [0.67 g, 1.72 mmol, 11% yield based on reacted lactone, 32% yield based on reacted phosphite, bp 110–115° (0.15 Torr)]. This liquid was not isolated in sufficient quantity or purity to allow complete characterization. However, the ir and pmr spectra of impure samples indicated that the structure of **9f** was analogous to **9d** which was obtained for tri-*n*-butyl phosphite and lactone: pmr (CDCl$_3$) δ 0.96 (9 H, t, J_{HH} = 7 Hz, CH_2CH_3), 1.21 (9 H, d, J_{HH} = 7 Hz, $CHCH_3$), 2.5 (6 H, broad m, CH_2), 1.55 (6 H, s, gem methyls), 1.53 and 1.78 (3 H each, d, J_{HP} = 3.0 and 1.5 Hz, vinyl methyls), 4.3 and 4.8 ppm (3 H, m, OCH); important ir bands occurred at 796, 868, 996, 1030, 1072, 1112, 1150, 1375, 1460, 1665 (w), 1725, and 2950 cm^{-1}. **9f** was converted into the thiophosphate **15f** by warming with sulfur. The thiophosphate decomposed on attempted trapping on vpc column B at 275°.

A large amount of viscous cloudy residue was left from the distillation which appeared to be analogous to the polymeric material obtained from triisopropyl phosphite and lactone. The ir spectrum of the viscous residue (neat film) showed absorptions at 800, 876, 926, 945, 969, 996, 1058, 1115, 1230, 1255, 1382, 1462, 1670 (w), 1730, 1750, and 2950 cm^{-1}.

Dimethyl Phenyl Phosphite.—Lactone (3.35 g, 23.9 mmol) and the phosphite (8.90 g, 47.8 mmol) were heated at 120°. After 408 hr vpc analysis showed 80% conversion of lactone into a number of products of which the two major products were present in 35 (**16h**) and 40% (**9h'**) yields (based on reacted lactone and calculated using vpc method B). The ratio of the two major products did not change appreciably during the course of the reaction. Also present were the methyl and phenyl esters of 2,2,4-trimethyl-3-oxovaleric acid in 2 and 15% yields, respectively (identified by comparison of retention times on vpc column A with those of authentic samples), and a number of unidentified products in very small yields. Distillation failed to separate the major products [35% combined yield, bp 70–80° (0.3 Torr)]. Warming of the impure fractions with methyl iodide converted **9h'** to **16h'** and did not affect **16h**. **16h** and **16h'** were separated and collected at 220° isothermal on vpc column B. See Table VI for spectral data.

Methyl Ethylene Phosphite.—Phosphite (2.87 g, 0.0205 mol) and **4** (5.00 g, 0.410 mol) heated at 110° for 369 hr resulted in 65% consumption of lactone. Vpc analysis showed two products in 15 (**17**) and 80% (**9g**) yield based on lactone consumed and using vpc method B. Distillation of 2.91 g of product solution gave fractions containing the two products in various ratios (0.78-g total, 61% yield, bp 82–86° (0.006 Torr)]. A fraction rich in **9g** was transesterified in benzene by an excess of methanol in 16 hr at 60° to methyl ethylene phosphite, methyl 2,4,4-trimethyl-3-oxovalerate, and trimethyl phosphite as shown by pmr and vpc analysis (columns A and B) of the reaction solution using authentic samples for comparisons.

The product mixture was warmed 2 hr with sulfur to give the thiophosphates **15g** and **17-S** which were separated by preparative vpc at 230°. **17-S** was a white solid (mp 103.5–105°): pmr (CDCl$_3$) δ 1.50 (3 H, s, gem CH_3), 1.62 (3 H, s, gem methyl), 1.70 (3 H, d, J_{HP} = 3.5, Hz, vinyl CH_3), 1.82 (3 H, d, J_{HP} = 5.0 Hz, vinyl CH_3), 3.70 (3 H, d, J_{HP} = 14 Hz, CH_3OP), 3.7 to 4.8 (4 H, broad m, OCH_2CH_2O); ir (film) 2950, 1740, 1670 (w), 1450, 1390, 1365, 1265, 1155, 1126, 1078, 1045, 960, 926, 880, 860, 842, 828, 788, 763 cm^{-1}. Data for **15g**, also a white solid, mp 84–85°, appear in Table VI. **17-S** and **15g** were subjected to quantitative elemental analysis as a mixture (see Table VI).

Dimethyl Methylphosphonite.—The phosphonite was prepared from methyl phosphonous dichloride[25] by reaction of the

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[24] G. Kamai and F. M. Kharrosova, *Tr. Kazan. Khim. Tekhnol. Inst.*, **23**, 122 (1957).

[25] B. J. Perry, J. B. Reesor, and J. L. Ferron, *Can. J. Chem.*, **41**, 2299 (1963).

latter with methanol in pentane in the presence of dimethylaniline. Lactone (0.15 g, 1.5 mmol) and methyl dimethylphosphonite (0.14 g, 1.5 mmol) were mixed neat under N_2. The reaction at room temperature, monitored by vpc, was complete in 48 hr. Volatiles were removed under vacuum at room temperature to leave reasonably pure (by pmr and vpc) **9i**: 0.25 g; 83% yield; pmr ($CDCl_3$) δ 1.35 (3 H, d, J_{HP} = 9 Hz, PCH_3), 1.33 and 1.36 (3 H each, s, $C(CH_3)_2C$), 1.49 (3 H, d, J_{HP} = 3.5 Hz, vinyl CH_3), 1.70 (3 H, d, J_{HP} = 1.5 Hz, vinyl CH_3). Treatment of **9i** with methyl iodide at 25° gave **16i**, isolated by preparative vpc.

Tri-*n*-butyl Phosphine.—Lactone **4** (10.0 g, 72 mmol) and the phosphine (18.5 g, 92.0 mmol) were heated at 100–120° for 2 weeks. On cooling, a light tan-colored solid precipitated from the dark brown reaction solution, 4.14 g, 41% yield, which was recrystallized from diglyme to give white powder, mp 193–195°. This was shown by spectral comparison to be identical with the polymer obtained on treatment of lactone with a trace of sodium methoxide (lit.[14] mp 198–200°). The polymer decomposed on melting to lactone.[14]

General Procedure for Reactions of Phosphites with Dione (3).—All reactions were run neat under N_2. Conditions and yields appear in Table I. Spectral, physical, and analytical data for products, all liquids or oils, appear in Table I. In all cases the reactions were monitored by vpc. At 150° (Table I), trimethyl phosphite gave only the product of Arbuzov isomerization, the phosphinate **10a**. However, when the reaction was run at 100° or in hexane at 120°, the unisomerized dimethylphosphonite **8a** was isolated. A solution of trimethyl phosphite 300 g, 2.42 mol) and the dione (85 g, 0.61 mol) heated at 100° for 30 days gave on distillation the phosphonite **8a**, a colorless liquid, bp 76–81° (0.03–0.05 Torr), 64.1 g, 0.243 mol (40% yield), along with 19.0 g (0.072 mol) of the phosphinate **10a**, (12% yield). See Table II for spectral and analytical data. Reaction of **8a** at room temperature with methyl iodide or when heated by itself for 9 hr at 150° converted **8a** into **10a**, mass spectrum 264 (parent). Both the trimethyl and triethyl phosphite reactions at 120° showed only the product **8a** and **8b** early in the reaction. Products **9a** and **9b** were formed in increasing proportions as the reactions progressed. The tri-*n*-butyl and triisopropyl phosphite reactions gave no vpc evidence for formation of **8c** or **8d** at any time.

Methyl Dimethylphosphonite.—**3** (0.15 g, 1.5 mmol) and phosphonite (0.14 g, 1.5 mmol) were heated neat under N_2 at about 80°. Vpc monitoring showed the reaction to be complete in 18 hr. Removal of volatiles under high vacuum gave **8i**, essentially pure by vpc, in quantitative yield: pmr ($CDCl_3$) δ 1.17 (3 H, d, J_{HP} = 7.5 Hz, PCH_3), 1.32 (6 H, d, J_{HP} = 12 Hz, $PC(CH_3)_2$), 1.37 (6 H, s, $(CH_3)_2CO$), 3.55 (3 H, d, J_{HP} = 13 Hz, $POCH_3$), 3.72 (3 H, s, CO_2CH_3). **8i** was converted with methyl iodide to the phosphine oxide for analysis.

Tri-*n*-butyl Phosphine.—A solution of dione **3** (5.0 g, 36 mmol) in the phosphine (8.3 g, 41 mmol) under nitrogen at 120° showed isomerization of **3** to **4** in 18 hr (vpc analysis). Polymerization of **4** then ensued.

Reactions of the Methylphosphinate (10a).—**10a** (4.0 g, 15 mmol) was refluxed with 30 ml of 10% aqueous NaOH for 8 hr. The reaction mixture was acidified and subjected to continuous ether extraction for a prolonged period. The ether was dried over Na_2SO_4 and removed to leave the phosphinic acid **14**: 2.8 g, 15 mmol (near-quantitative yield); a white solid; mp 62–64°; recrystallized from ethanol, mp 71.4–72.8°; pmr (CCl_4) δ 1.06 (6 H, d, J_{HH} = 6.5 Hz, $CH(CH_3)_2$), 1.40 (3 H, d, J_{HP} = 14 Hz, PCH_3), 1.47 (6 H, d, J_{HP} = 15.5 Hz, $C(CH_3)_2P{=}O$), 3.30 (1 H, sep, J_{HH} = 6.5 Hz, $CH(CH_3)_2$), 12.3 (1 H, s, POH); ir ($CHCl_3$) 2980, 2940, 2880, 2100–2800 (w, broad, POH), 1696, 1468, 1375, 1296, 1170, 1090, 1045, 1028, 1002, 963, 883, 720 cm^{-1}.

Anal. Calcd for $C_8H_{17}O_3P$: C, 50.0; H, 8.9; P, 16.1. Found: C, 49.8, 49.7; H, 8.9, 9.0; P, 16.1, 16.5.

10a (16 g, 0.061 mol) was shaken at room temperature with 120 ml of 10% aqueous NaOH, during which time the temperature of the solution rose to 40°. The solution was acidified and ether extracted. The dried ether layer on evaporation yielded 6.0 g of an oil (**12**) which crystallized on standing. The mother liquor was then subjected to a continuous ether extraction. The dried ether solution, cooled to −20°, gave another 2.9 g of crystals (**12**): total yield 8.9 g, 0.35 mol (57%); mp 119.4–120.0°; neut equiv 250 (theory 252); pK_a 3.3 (H_2O, 25°); pmr ($CDCl_3$) δ 1.42 (6 H, s, $OC(CH_3)_2CO$), 1.56 (6 H, d, J_{HP} = 16 Hz, $(CH_3)_2CP{=}O$), 1.68 (3 H, d, J_{HP} = 14.5 Hz, PCH_3), 3.74 (3 H, d, J_{HP} = 10.5 Hz, $POCH_3$), 11.4 (1 H, s, CO_2H); ir (KBr) 2990, 2500–3600 (CO_2H), 1710, 1692, 1467, 1407, 1390, 1366, 1307, 1260, 1200, 1170, 1150, 1130, 1052, 1030, 1002, 957, 890, 810, 762, 720 cm^{-1}.

Anal. Calcd for $C_{10}H_{19}O_5P$: C, 48.0; H, 7.6; P, 12.4. Found: C, 48.0; H, 7.4; P, 12.3.

12 was decarboxylated on heating at 150° to a colorless liquid with spectral properties consistent with the structure **13**: mass spectrum *m/e* (intensity, >15% base peak), 206 (parent, 5), 136 (100), 135 (60), 94 (45), 93 (22), 79 (17), 63 (15), 43 (35), 41 (29), 27 (19), and 15 (16); pmr (CCl_4) δ 1.02 (6 H, d, J_{HH} = 6.5 Hz, $HC(CH_3)_2$), 1.35 (3 H, d, J_{HP} = 13.5 Hz, PCH_3), 1.39 (6 H, d, J_{HP} = 15 Hz, $C(CH_3)_2P$), 3.31 (1 H, m, J_{HH} = 6.5 Hz, $HC(CH_3)_2$), 3.69 (3 H, d, J_{HP} = 10.5 Hz, $POCH_3$); ir (CCl_4), 2974, 2942, 1700, 1470, 1375, 1295, 1225, 1045, 1000, 888 cm^{-1}

When **10a** (3.0 g, 12 mmol) was refluxed 72 hr with 5 ml of 1:1 (v/v) $HCl–H_2O$, a water-insoluble layer appeared atop the reaction mixture. This layer was separated by addition of ether without shaking. The ether layer was dried (Na_2SO_4), and removal of the ether gave 0.70 g, 6.1 mmol (50% yield), of diisopropyl ketone identified by mass spectral, infrared, and vpc comparisons with authentic ketone. Extraction of the water layer with several portions of ether yielded 0.1 g (0.49 mmol) of **14**.

Yield of 8a, 9a, and 10a as a Function of Time.—A solution containing **3** (0.90 g, 64 mmol) and trimethyl phosphite (1.0 g, 81 mmol) in 2.0 ml of *n*-heptane was sealed under nitrogen in several glass tubes which were heated at 150°. Tubes were removed at intervals and their contents monitored from time to time by vpc analysis on column A. A set of identical samples was heated at 120°.

Reaction of Trimethyl Phosphite and Tris(dimethylamino)-phosphine with 2,2,4,4-Tetramethylcyclobutanone.—A 1-mol excess quantity of phosphite and the lactone were heated without solvent for 3 weeks at 115°. No detectable starting material consumption or product formation could be detected by vpc. A similar reaction with the aminophosphine produced some cloudiness in the solution but no detectable product.

Reaction of Trimethyl Phosphite and Tris(dimethylamino)-phosphine with 3-Dicyanomethylene-2,2,4,4-tetramethylcyclobutanone.—Reaction with excess phosphine at 120° for 15 days and excess aminophosphine at 60° for several weeks gave complete consumption of both butanone and phosphorus reactant. The reactions became very dark colored. However, no products were detected by vpc.

Effect of Time and Solvent on 9b/8b Ratio.—Dione **3** (0.35 g, 2.5 mmol) and triethyl phosphite (0.50 g, 3.0 mmol) were mixed in four different tubes and sealed under nitrogen. In another set of tubes the same amounts of phosphite and dione were mixed with 1 ml of acetonitrile and sealed under nitrogen. In a third set of tubes, *n*-heptane was used in place of acetonitrile. All were placed in a bath at about 150°. At intervals, tubes were removed and their contents analyzed by vpc, column A. For analysis the contents of the tube were transferred to a 5-ml volumetric flask and to dissolve all dione were diluted to 5 ml with acetonitrile for the neat and acetonitrile experiments and with chloroform for the heptane experiments. The diluted solution (1 ml) was then mixed with 40 μl of decane as internal standard. This allowed a reasonably accurate determination of the per cent dione unreacted. Results appear in Table III.

Conversion of 8b to 9b.—A mixture of 7.0 g of **3** with 10 ml of triethyl phosphite was sealed under N_2 and heated at about 150° for 92 hr. During this time the contents of the tube were shaken at intervals to dissolve the dione which sublimes on to the sides of the tube. After removal of dione and phosphite under high vacuum, the residue was shown to contain only **8b** and **9b** in 1.98:1.00 ratio. Portions of this mixture were sealed under nitrogen and kept at room temperature, 120 or 150°. At intervals a tube was removed, and vpc analysis for ratio **9b**/**8b** carried out. Results appear in Table IV.

To one of the above samples which had been at room temperature for 1 week (**8b**/**9b** = 1.5), a portion of decane was added as internal standard, and the tube was resealed and heated at 150°. Relative areas of peaks assigned to **8b**, **9b**, and triethyl phosphite relative to decane of assumed area 1.0 also appear in Table IV. Large amounts of dione were also formed but reliable quantitative data could not be obtained, since **3** crystallized out of the reaction mixtures at room temperature. The figures in Table IV are based on soluble dione only. A small portion of **4** was also formed in each case, amounting to about 6% of the area of the internal standard.

Registry No.—**3**, 32687-47-1; **4**, 32687-48-2; **8a**, 32674-59-2; **8b**, 32674-60-5; **8e**, 32674-61-6; **8f**, 32674-62-7; **8i**, 32674-63-8; **9a**, 14261-54-2; **9b**, 14261-50-8; **9c**, 32674-66-1; **9d**, 14261-51-9; **9e**, 32674-68-3; **9f**, 32674-69-4; **9g**, 32674-70-7; **9i**, 32674-71-8; **10a**, 32674-72-9; **10b**, 32674-73-0; **10e**, 32674-74-1; **10f**, 32674-75-2; **10h**, 32674-76-3; **10i**, 32674-77-4; **11e**, 32674-78-5; **12**, 32674-79-6; **13**, 32674-80-9; **14**, 32722-86-4; **15c**, 32674-81-0; **15d**, 32674-82-1; **15e**, 32674-83-2; **15f**, 32674-84-3; **15g**, 32674-85-4; **16b**, 32674-86-5; **16h**, 32674-87-6; **16h′**, 32674-88-7; **16i**, 32674-89-8; **17-S**, 32674-90-1; methyl ethylene phosphite, 32674-91-2; dimethyl phenyl phosphite, 32674-92-3.

Pentacovalent Phosphorus. II. Reactions of Dione and Lactone Dimers of Dimethylketene with Trivalent Phosphorous Acid Amides[1]

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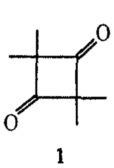
Reactions of the dione **1** and lactone **2** dimers of dimethylketene with the phosphoramidites $(CH_3O)_2PN(CH_3)_2$ (**3**), $CH_3OP[N(CH_3)_2]_2$ (**4**), and $C_6H_5OP[N(CH_3)_2]_2$ (**5**) and with trisdimethylaminophosphine (**6**) were investigated. Carboxy esters resulted from reactions of **3** and **4** with either dimer while **5** and **6** gave carboxamides. The structures of these products are similar to those formed from dimethylketene dimers on reaction with trialkyl phosphites. Except for reactions of **3**, identical products were formed from either **1** or **2** and a given phosphorus derivative. On reaction of **1** and **3**, three products are formed in relative proportions dependent on reaction temperature. These reactions are discussed in terms of a postulated mechanism involving nucleophilic attack by phosphorus on carbonyl carbon of **1** or **2**, followed either by ring expansion to a cyclic pentacovalent phosphorus intermediate or by ring opening to a phosphonium enolate species. Isomerization of **1** to **2** in the presence of **5** or **6** is also accommodated by the suggested reaction series. Possible kinetic control of carboxamide *vs.* carboxy ester formation is treated in terms of the structures and reaction patterns predicted for the postulated pentacovalent intermediates.

In the preceeding paper[3] we reported reactions of trialkyl phosphites and dimethyl methylphosphonite with the dimers (**1** and **2**) of dimethylketene. These results were interpreted in terms of transient pentacovalent phosphorus intermediates formed *via* ring expansion of the initial dimer–trivalent phosphorus adduct. Ultimate product formation was postulated to proceed *via* migration of an alkoxy group from pentacovalent phosphorus to the adjacent carbonyl group. Of interest in this regard is the question of the apparent relative migrational preference of different phosphorus substituents. This paper reports results of reactions of **1** and **2** with phosphorus amides having both methoxy and dimethylamino groups on phosphorus in the same molecule.



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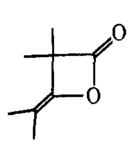

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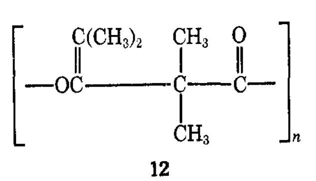

$$\left[-\mathrm{O}\overset{\mathrm{C(CH_3)_2}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\overset{|}{\underset{|}{\mathrm{C}}}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\right]_n$$

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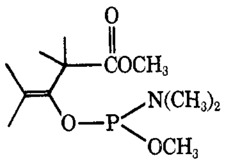
Results

Reactions were carried out neat under nitrogen. The trivalent phosphorus derivatives used (**3**–**6**) are shown in Table I in which products and yields are also recorded for the lactone reactions. The lactone reactions proceeded in a rather straightforward manner giving reasonably high yields of vinyl products **7**–**11** similar to those which result with the trialkyl phosphites, as either the carboxamide or carboxylic ester. A side product in several instances is the same polymer **12** formed from lactone under the influence of methoxide.[4]



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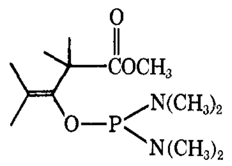

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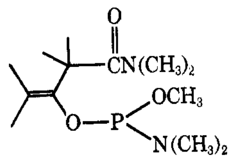

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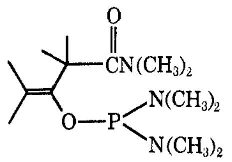

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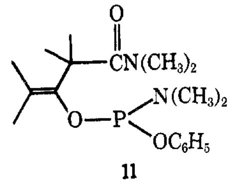

11

Reactions of the mixed amide esters, phosphoramidites $(CH_3O)_2PN(CH_3)_2$ and $CH_3OP[N(CH_3)_2]_2$, gave almost exclusively carboxyl ester products. Only with the diamino compound **4** at 115° is any carboxamide **9** formed. By contrast $C_6H_5OP[N(CH_3)_2]$ yields exclusively the carboxamide **11**. Evidence for the structures of products **7**–**11** is given by their nmr and ir spectra and those of the sulfur and Arbuzov products (Table II). All show a weak ir band at about 1665 cm^{-1} for

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[2] National Institutes of Health Predoctoral Fellow, 1966–1969. This work taken in part from the Ph.D. Thesis of W. D. Johnson, University of Utah, 1969.

[3] W. G. Bentrude, W. D. Johnson, W. A. Khan, and E. R. Witt, *J. Org. Chem.*, **37**, 631 (1972).

[4] R. H. Hasek, R. D. Clark, E. U. Elam, and J. C. Martin, *ibid.*, **27**, 60 (1962).