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THE PREPARATION OF SOME CYCLIC PHOSPHONATES AND THEIR USE IN OLEFIN SYNTHESIS

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Abstract—The preparation and the use in olefin synthesis of two 5-membered cyclic phosphonates, 2-carbethoxymethyl-4,5-dimethyl-2-oxo-1,3,2-dioxaphospholane (**4b**) and 2-cyanomethyl-4,5-dimethyl-2-oxo-1,3,2-dioxaphospholane (**4c**) and the 6-membered phosphonates, 2-carbalkoxymethyl-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanes (**5a** and **5b**) and 2-cyanomethyl-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane (**5c**) are described. Reactions of **4b** with aromatic and aliphatic aldehydes lead to preferential formation of *cis*-olefins. Reactions of the other cyclic phosphonates with aldehydes lead to various mixtures of *cis* and *trans* olefins.

In our preliminary communication we reported that reactions of a 5-membered cyclic phosphonoacetate (**4b**) with aldehydes lead to preferential formation of *cis*-olefins.[1] In order to facilitate further exploration of this discovery it was necessary to develop a convenient method applicable for routine preparation of large quantities of 5-membered cyclic phosphonates (and for comparison 6-membered ones) suitable for olefin synthesis.

In this paper we describe the preparation of such phosphonates, and results from their reactions with representative aldehydes under various conditions.

RESULTS

Preparation of phosphonates. There are numerous reports in the literature dealing with the preparation of cyclic phosphonates,[2–8] however, only one of these describes the preparation of compounds suitable for Wittig-type olefin synthesis. Thus preparation of 2 - carbethoxymethyl - 2 - oxo - 1,3,2 - dioxophospholane, and some other derivatives, was reported by reacting polymeric ethyl phosphonoacetate with epoxides in a sealed tube.[4] As this method did not seem to be readily applicable to large scale routine laboratory preparations, we studied two other approaches: (1) Reaction of a diol with a phosphonodichloride[7] and (2) Arbusov reaction of cyclic phosphites with an α-halogenoacetic derivative.

Experiments according to the first approach in which carbethoxymethylphosphonodichloride (**1**)[4] was reacted with ethylene glycol and 1,2-propanediol gave undistillable products. Phosphonodichloride **1** failed to react with pinacol and catechol but reacted with 2,3-butanediol (mixture of *meso* and *racemic*) and with 2,2 - dimethyl - 1,3 - propanediol to give the expected phosphonates in low yields. The second approach proved to be more fruitful. Although it is well recognised that in the Arbusov reaction ring-opening often competes considerably with the formation of cyclic phosphonates,[2,3] phosphites derived from highly substituted diols afford the cyclic phosphonate as the main product.[3,5,6,8]

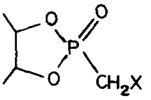
Cyclic phosphites 4,5 - dimethyl - 2 - methoxy - 1,3,2 - dioxaphospholane[9] (**2**) (mixture of *meso* and *racemic*), and 5,5 - dimethyl - 2 - methoxy - 1,3,2 - dioxaphosphorinane[5,8] (**3**) were obtained by transesterification with trimethylphosphite.

Arbusov reaction of **3** with chloroacetic esters and chloroacetonitrile gave the cyclic phosphonates **5a**, **5b** and **5c** in high yields. In contrast, phosphite **2** reacted only sluggishly with ethyl chloroacetate affording an impure product in low yield. However, reactions of **2** with ethyl bromoacetate or chloroacetonitrile gave the desired 5-membered cyclic phosphonates **4b** and **4c** respectively, as mixtures of the *racemic* and *meso* isomers (suitable for synthetic use).

Gas chromatographic examination of **2**, prepared from a commercial mixture of *meso* and *racemic* 2,3-butanediol, revealed the presence of three isomers. By fractional distillation over a spinning band column we obtained two fractions, one of which contained mainly *racemic* **2** and another containing mainly one of the *meso* compounds,[9] Arbusov reaction of these phosphites with ethyl bromoacetate afforded pure dl and one of the *meso* isomers of **4b**. The stereochemistry around the phosphorus in this *meso* compound is presently unknown.

Physical constants of the cyclic phosphonates are listed in Table 1.

Olefin syntheses. Phosphonates **4b**, **4c**, **5b** and **5c** were reacted with a series of aldehydes under various conditions. The mixtures of unsaturated esters or unsaturated nitriles, which were obtained in yields of 70–80%, were analyzed by gas chromatography. A pure sample of each



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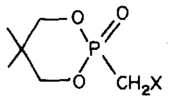

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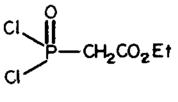
a, $X=CO_2CH_3$
b, $X=CO_2C_2H_5$
c, $X=CN$



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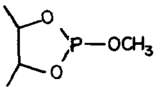

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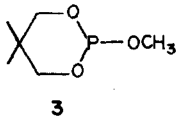

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Table 1. Yields and physical constants of cyclic phosphonates

Phosphonate	Yield (%)	B.p./torr	M.p. or n_D^{20}	IR (cm^{-1})	^1H NMR ($CDCl_3$) (δ ppm)	^{31}P NMR (ppm)†	Empirical formula mol. weight (Calc.)	Mol. weight found (MS)	Anal.	
									Calc.	Found
4b *meso* + dl	75	135°/0.3	1.4550	1720 1270	5.1–4.5(m), 4.52–4.0(m), 3.17(d, J_{PCH} = 22.5 Hz), 3.15(d, J_{PCH} = 22.5 Hz), 1.47–1.04(m).	31.8§ 32.2§	$C_8H_{15}O_5P$ 222.1	222	C, 43.24 H, 6.75	43.05 6.63
4b *meso*	75	130°/0.1	1.4505	1720 1270	5.00–4.43(2Hm), 4.43–4.0 (2Hq), 322(2H, d, J_{PCH} = 22.5 Hz), 1.47–1.04(9H, m)	32.2§	$C_8H_{15}O_5P$ 222.1	222		
4b dl	75	126°/0.1	1.4480	1720 1270	4.73–4.0(4Hm), 3.17(2Hd J_{PCH} = 22.5 Hz), 1.45–1.04 (9Hm)	31.8§	$C_8H_{15}O_5P$ 222.1	222		
4c *meso* + dl	50	119°/0.1	1.4530	2260 1250	5.05–4.15(m), 3.22(d, J_{PCH} = 22.5 Hz), 3.21(d, J_{PCH} = 22.5 Hz), 1.52–1.42(m)	30.05‡	$C_6H_{10}NO_3P$ 175	175	C, 41.14 H, 5.71 N, 8.00	40.69 5.91 8.04
5a	82		84°	1730 1260	4.22–4.0(4H, m), 3.75(3H, s) 3.0(2H, d, J_{PCH} = 22.7 Hz), 1.12(3H, s), 1.0(3H, s)		$C_8H_{15}O_5P$ 222.1	222	C, 43.24 H, 6.75	43.40 6.84
5b	85	160°/05	59°	1710 1250	4.4–4.0(6H, m), 3.04(2H, d, J_{PCH} = 22.5 Hz) 1.25(3H, t) 1.1(3H, s), 1.02(3H, s).	12.1‡	$C_9H_{17}O_5P$ 236.2	236	C, 45.76 H, 7.20	45.92 7.19
5c	72	166°/0.2	126°	2250 1270	4.25(4H, d, J_{PCH} = 10 Hz), 3.06(2H, d, J_{PCH} = 22.5 Hz), 1.16(3H, s), 1.09(3H, s)	7.82‡	$C_7H_{12}NO_3P$ 189.1	189	C, 44.44 H, 6.38 N, 7.40	44.42 6.65 7.33

†Downfield from 85% H_3PO_4 as external standard.
‡In 1,2-dimethoxyethane.
§In tetrahydrofuran.

product was isolated by preparative gas chromatography, and structures were assigned on the basis of NMR and IR spectra. Results from the reactions of phosphonates with aldehydes are listed in Tables 2 and 3. The physical constants of the olefins obtained are listed in Table 4.

Examination of Table 2 reveals that reactions of **4b** with aldehyde, leads to the formation of *cis*-olefins in excess over the *trans*-isomers. Benzaldehyde was reacted with **4b** under four different conditions giving the same *cis*/*trans* ratio. It is also worthy of note that aliphatic and aromatic aldehydes give approximately the same isomer distribution. In contrast to **4b** reactions of **4c** give predominantly *trans* olefin.

The results from the reactions of the 6-membered cyclic phosphonates are listed in Table 3. From Table 3 it can be seen that reactions of **5b** and **5c** give a higher *cis*/*trans* ratio with aliphatic aldehydes than with aromatic ones. The use of Li^+ as a counter ion in this series causes a considerable raise in the *cis*/*trans* ratio (except Table 3, exp. 4, X=CN) reaching in one case (Table 3, exp. 4, X=CO_2Et) the proportion of *cis* product obtained in the reactions of **4b**. In contrast, reactions of **4b** and **4c** are unaffected by changing the counter ion from sodium to lithium.

Table 2. Isomer distribution in reactions of aldehydes with five-membered cyclic phosphonates **4b** and **4c**†

No.	R in RCHO	Base	Solvent	R–CH=CH–X X=CO_2Et *Z*/*E*	 X=CN *Z*/*E*
1	Ph	NaH	DME	60/40‡	40/60
2	Ph	BuLi	THF	65/35	40/60
3	Ph	NaOEt	EtOH	60/40	—
4	Ph	$Bu_4N^+OH^-$	CH_2Cl_2/H_2O	60/40	—
5	i-Pr	NaH	DME	68/32	30/70
6	i-Pr	BuLi	THF	65/35	25/75
7	n-Pr	NaH	DME	52/48	30/70
8	Et	NaH	DME	55/45	—

†All experiments were carried out using mixtures composed of racemic and *meso* phosphonates, **4b** and **4c**, prepared from commercially available 2,3-butanediol via phosphite **2**.

‡Identical results were obtained when this experiment was repeated using either pure racemic or *meso* **4b**.

Table 3. Isomer distribution in reactions of aldehydes with 6-membered cyclic phosphonates **5b** and **5c**

No.	R in RCHO	Base	Solvent	R–CH=CH–X X=CO_2Et *Z*/*E*	 X=CN *Z*/*E*
1	Ph	NaH	DME	5/95	5/95
2	Ph	BuLi	THF	29/71	22/78
3	i-Pr	NaH	DME	43/57	43/57
4	i-Pr	BuLi	THF	62/38	30/70
5	n-Pr	NaH	DME	41/59	48/52

DISCUSSION

In contrast to the Wittig reaction with non-stabilized ylids, the phosphonate modification of the Wittig reaction[10] is known to lead predominantly to *trans* olefins.[11] Attempts to increase the proportion of the *cis* olefin formed in these reactions have been unsuccessful[12,13] excepting some reactions of phosphono ylids leading to trisubstituted olefins.[14,15] It is generally accepted that the predominant formation of *trans* olefins in this reaction is a result of thermodynamic control upon the reversible formation[16] and interconversion of the *erythro* and *threo* betaine (**6a** and **6b**) and their decomposition to

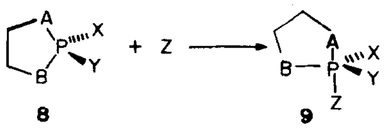
Table 4. Physical constants of olefins R–CH^2=CH^1–X

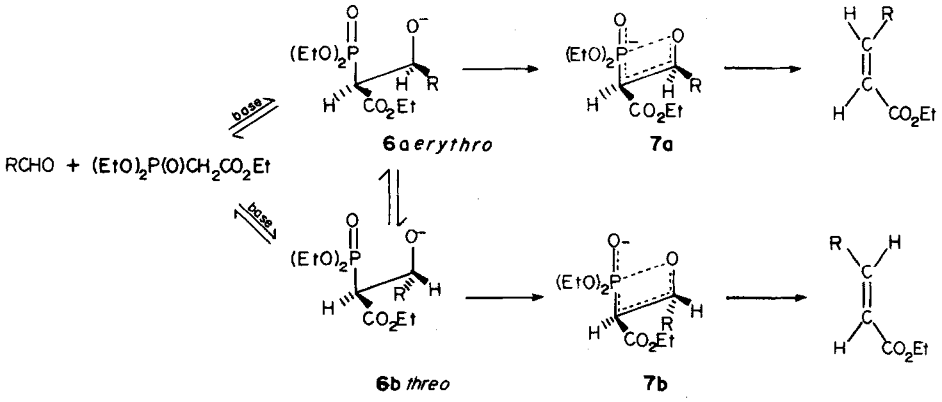
	Olefin R	X	IR (cm^{-1})	^{1}H NMR (CDCl$_3$) δ ppm H^1	^{1}H NMR (CDCl$_3$) δ ppm H^2	B.p./torr observed	B.p./torr in lit.	Lit.
(*Z*)	Ph	CO$_2$Et	1720, 700	5.92 (d, J = 13.5 Hz)	6.95 (d, J = 13.5 Hz)	108°/5[a]	157°/25	[b]
(*E*)	Ph	CO$_2$Et	1720, 990	6.40 (d, J = 16 Hz)	7.70 (d, J = 16 Hz)			
(*Z*)	Ph	CN	2210, 780	5.04 (d, J = 12 Hz)	7.01 (d, J = 12 Hz)	123°/10[a]	139°/30	[c]
(*E*)	Ph	CN	2210, 970	5.83 (d, J = 16 Hz)	7.33 (d, J = 16 Hz)			
(*Z*)	i-Pr	CO$_2$Et	1710, 720	5.62 (d, J = 12 Hz)	6.02 (dd, J = 12 Hz and J = 10 Hz)	58°/10[a]	62–64°/11	[d]
(*E*)	i-Pr	CO$_2$Et	1710, 980	5.77 (d, J = 15 Hz)	6.95 (dd, J = 15 Hz and J = 6.5 Hz)			
(*Z*)	i-Pr	CN	2220, 740	5.20 (d, J = 11 Hz)	6.32 (dd, J = 11 Hz and J = 12 Hz)	40°/10[a]	68°/34	[e]
(*E*)	i-Pr	CN	2220, 980	5.27 (d, J = 16 Hz)	6.73 (dd, J = 16 Hz and J = 6 Hz)			
(*Z*)	n-Pr	CO$_2$Et	1720, 810	5.75 (d, J = 12 Hz)	6.25 (dt, J = 12 Hz and J = 7 Hz)	61°/12[a]	73°/15	[f]
(*E*)	n-Pr	CO$_2$Et	1720, 980	5.92 (d, J = 16 Hz)	7.10 (dt, J = 16 Hz and J = 7 Hz)			
(*Z*)	n-Pr	CN	2220, 720	5.38 (d, J = 14 Hz)	6.60 (dt, J = 14 Hz and J = 7.5 Hz)	57°/10[a]	60°/17	[g]
(*E*)	n-Pr	CN	2220, 970	5.37 (d, J = 17 Hz)	6.80 (dt, J = 17 Hz and J = 7.5 Hz)			
(*Z*)	Et	CO$_2$Et	1720, 730	5.83 (d, J = 12 Hz)	6.38 (dt, J = 12 Hz and J = 6 Hz)	55°/15[a]	147°/760	[h]
(*E*)	Et	CO$_2$Et	1720, 980	5.83 (d, J = 16 Hz)	7.00 (dt, J = 16 Hz and J = 6 Hz)		158°/760	[i]

[a] B.p. of (*E*) and (*Z*) mixture obtained in the reaction. [b] K. Kindler, *Lieb. Ann.* **452**, 112 (1927). [c] G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.* **58**, 2428 (1936). [d] H. Schinz and E. Rossi, *Helv. Chim. Acta* **31**, 1962 (1948). [e] R. M. Ross and M. L. Burnett, *J. Am. Chem. Soc.* **71**, 3562 (1949). [f] B. R. Baker, M. V. Guerry, R. S. Safir and S. Bernstein, *J. Org. Chem.* **12**, 144 (1947). [g] R. A. Letch and R. P. Linstead, *J. Chem. Soc.* 613 (1933). [h] E. Schjanberg, *Svensk. Kem. Tidskr.* **50**, 102 (1938); *Chem. Abstr.* **32**, 7016 (1938). [i] E. Schjanberg, *Z. Phys. Chem.* **178**, 276 (1936); *Chem. Abstr.* **31**, 4196 (1937).

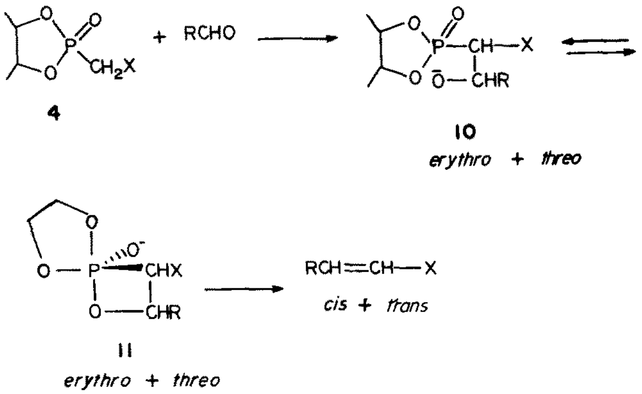
olefins.[17,18] Kinetic[19] and low temperature ^{31}P NMR studies[20,21] of the Wittig reaction indicate the involvement of a 4-membered heterocyclic oxaphosphetane of type **7** as an intermediate, however, there is no evidence, so far, for the formation of such an oxaphosphetane intermediate in the phosphonate or phosphinoxy modification.[21]

It is possible to rationalize the formation of considerable amounts of *cis*-olefins in the reactions of the 5-membered cyclic phosphonates in terms of ring strain in the 5-membered dioxaphospholane ring. 5-Membered ring phosphorus compounds of several types with tetrahedral phosphorus (**8**) react faster than their acyclic analogs in reactions leading to pentacoordinate intermediates (**9**). This has been attributed[22–25] mainly to release of ring strain upon passing from the tetrahedral to the trigonal bipyramid structure in which the 5-membered ring occupies an apical-equatorial orientation (e.g. **8**→**9**). 5-Membered tetracoordinated phosphorus compounds have been reported[26] to enter readily into reactions that lead to the formation of stable spirophosphoranes.[27] Therefore it seems reasonable to assume that *erythro* and *threo* betaines, **10**, formed in the reactions of **4** undergo rapid ring closure to oxaphosphetanes **11**, since this will be accompanied by release of ring strain in the 5-membered ring. Furthermore, spirophosphorane **11**





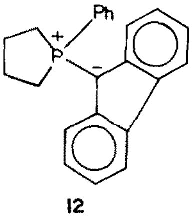
thus formed would be expected to be very favorable since both the 5- and 4-membered rings prefer occupying apical-equatorial over diequatorial positions, while the oxide anion prefers considerably the equatorial orientation over the axial one.[22,27] Increased stability of the intermediate would result in lower rates of decomposition to starting materials and of interconversion of *threo* and *erythro* intermediates, and consequently, in the formation of considerable amounts of *cis* olefin.



In recent years, a number of 5-membered cyclic phosphorus ylids: **12**,[19] **13**,[28] **14**,[29] **15** and **16**,[30] have been described. Reactions of these with the exception of **15b** gave only low proportions of *Z* olefins. The predominant formation of *E* olefins by these ylids indicate high degree of reversibility in the reactions as compared to that of **4b**. It is possible that this is due to the lower stability of spirophosphorane intermediates derived from **12–16** relative to **11**, since in the formers, C atoms of low apicophilicity are forced into apical position. It has been noted that 5-membered rings containing at least one oxygen bonded to phosphorus highly prefer the apical-equatorial disposition.[31,32] However, compound **17**, pseudorotates at room temperature, but on cooling, it adopts a structure in which the ring is diequatorially oriented.[33] Such diequatorial orientation of the 5-membered ring in the spirophosphorane intermediates derived from **12–16** would force the oxide anion to become apical, which is also highly unfavorable.[25]

Furthermore, examination of the results in Table 2 reveals that the reaction of benzaldehyde and **4b** can be carried out, without change in the stereochemistry, using sodium ethoxide in ethanol indicating that the cyclic phosphonate does not suffer ring opening prior to its reaction with the aldehyde.† Experiment 4 in Table 2 indicates the applicability of phase transfer catalysis to the reactions of **4b** without affecting the stereochemical outcome.[35]

Further examination of the results listed in Tables 2 and 3 reveals that changing the cation from sodium to lithium causes a singificant increase in the proportion of *cis* olefin in the reactions of the 6-membered phosphonates **5b** and **5c** but has no effect upon the reactions



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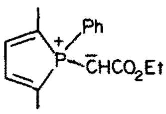

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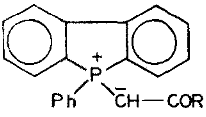

R = Ph, OCH_3, OC_2H_5

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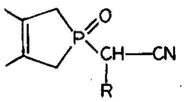
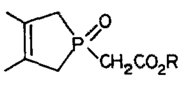


a, R=H
b, $R=CH_3$

15



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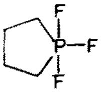

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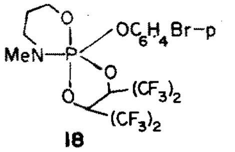

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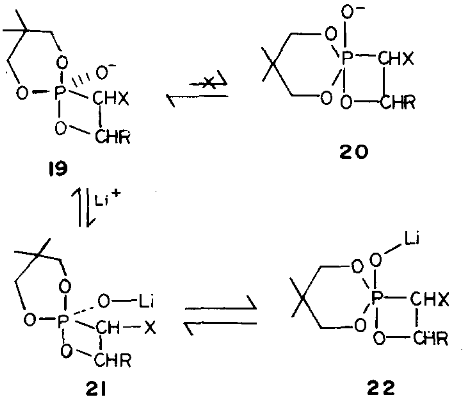
†In contrast to this, however, we have observed ring opening in some reactions of cyclic phosphonates with nitrones in protic solvents.[34]

of the 5-membered phosphonated **4b** and **4c**. This is in contrast with the known influence of the lithium cation in increasing the proportion of the *trans* olefin formed in reactions of the other phosphorus ylids.[11,12,15] This is attributed to increase in the reversibility factor due to lowering the energies of both the ylid and the betaine as a consequence of their association with the lithium.

Our results can be rationalized by assuming that the lithium has a stabilizing effect on the spirophosphorane intermediate derived from **5b** and **5c**. Calculations have indicated a preference of the 6-membered phosphorinan ring for a diequatorial position in a trigonal bipyramide.[36] However, when the 6-membered ring contains heteroatoms attached to the phosphorus, lone pair orientation effects have to be taken into account. The preference for the oxygen lone pairs to be oriented in the equatorial plane[37] makes an apical-equatorial boat conformation more favored than both a diequatorial and an apical-equatorial chair conformation.[38] Indeed, the results of a recent X-ray analysis of **18** showed that the oxazaphosphorinane ring is an apical-equatorial boat conformer. We assume that an apical-equatorial boat conformer **19** would be less stable than **18**, due to non-bonded 1,4 interactions of the *gem*-dimethyl groups, therefore a diequatorial chair conformation may be preferred.[39] The attainment of such an orientation (**20**) may be hindered by the negatively charged P–O⁻. Lithium cation due to its small size, has a very high polarizing power and great tendency toward covalent bond formation. Therefore, it is reasonable to assume that covalent bond formation between the lithium cation and the oxide anion in **19** would lead to a more stable intermediate by allowing the attainment of diequatorial orientation by the 6-membered ring, **22** (via **21**).



19 20 21 22

On the basis of the present results, it is difficult to interpret the observed lower proportion of *cis* olefin formed from **4c** as compared to **4b**, and the formation of particularly low yields of *cis* olefins from the 6-membered phosphonates with benzaldehyde. Further work using a wider variety of phosphonates and of carbonyl compounds is now in progress in our laboratory.

EXPERIMENTAL†

Preparation of 2 - cyanomethyl - 4,5 - dimethyl - 2 - oxo - 1,3,2 - dioxaphospholane (**4c**) *and of 5,5 - dimethyl - 2 - oxo - 1,3,2 - dioxaphosphorinane derivatives* (**5a–c**). A mixture of one mole of cyclic phosphite (**2**[9] or **3**[5,6]) and 1.5 mole of chlorocompound was heated under reflux in an oil bath at 145° for 16 hr. The products were isolated by distillation, except for **5a** which was obtained directly by recrystallization from benzene.

2 - Carbethoxymethyl - 4,5 - dimethyl - 2 - oxo - 1,3,2 - dioxaphospholane (**4b**). A round bottomed flask, equipped with a reflux condenser, containing a mixture of 1 mole of **2** and 1.5 mole of ethyl bromoacetate was dipped into an oil bath preheated to 160°. A vigorous reaction commenced immediately. The mixture was kept at this temp. for 4 hr. The product was isolated by distillation.

Reactions of aldehydes with phosphonates

(A) *With sodium hydride in 1,2-dimethoxyethane.* 2.4 g (0.05 mol) of 50% dispersion of NaH in mineral oil was washed with petroleum ether 40°–60° (3 × 10 ml) in an inert atmosphere. After evaporation of the residual petroleum ether 30 ml of 1,2-dimethoxyethane (DME, freshly distilled from LAH) was injected, followed by a solution of 0.05 mol phosphonate in 30 ml DME. After the liberation of H_2 ceased, a soln of 0.05 mol aldehyde in 20 ml DME was introduced slowly with cooling. The reactions were stirred for 3 hr at room temp. and decomposed by the addition of water and ether. The products were isolated by ether extraction followed by drying and distillation. Thw (*Z*)/(*E*) ratios of the product mixtures obtained were determined by glc on a 12 ft × 0.25 in. 10% Apiezon L on Diatoport 60–80 column at temp. ranging from 90° to 210°. A pure sample of each geometrical isomer was isolated by preparative glc and structures were assigned on the basis of IR and NMR spectra. B.ps of the product mixtures as well as the relevant spectral data of each product are listed in Table 4.

(B) *With butyllithium in tetrahydrofuran.* Into a soln of 0.01 mole phosphonate in 10 ml dry THF cooled to −78° in an inert atmosphere was injected 4.3 ml of a 15% soln of n-BuLi in hexane (0.01 mol). To this soln was introduced a soln of 0.01 mol aldehyde in 5 ml THF. The mixture was stirred at room temp. for 3 hr and analyzed by gc.

(C) *With phase transfer catalysis.* A soln of 5.5 g (0.025 mole) **4b** and 2.65 g (0.025 mol) benzaldehyde in 10 ml dichloromethane was added with stirring to a mixture composed of 20 ml CH_2Cl_2, 20 ml 50% NaOH aq., and 0.322 g, 0.001 mole) of tetrabutylammonium bromide. The mixture was stirred and refluxed for 30 min, the phases separated, washed and dried as usual. After removal of the solvent the product was distilled and analyzed by gc.

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REFERENCES

[1] E. Breuer and D. M. Bannet, *Tetrahedron Letters* 1141 (1977).
[2] A. E. Arbusov and N. A. Ragumova, *Izverst. Akad. Nauk. S.S.S.R. Otd. Khim. Nauk.* 1061 (1968); *Chem. Abstr.* **53**, 3046 (1959).
[3] G. Aksnes and R. Eriksen, *Acta Chem. Scand.* **20**, 2463 (1966).
[4] K. A. Petrov and L. V. Khorkhoyann, *Khim. Org. Soedin. Fosfora. Akad. Nauk. S.S.S.R., Otd. Obsh. Tekh. Khim.* 176 (1967); *Chem. Abstr.* **69**, 67480 (1968).
[5] L. Maier, *Syn. Reac. Inorg. Metal-Org. Chem.* **6**, 133 (1976).
[6] B. Costisella and H. Gross, *J. Prakt. Chem.* **314**, 532 (1972).

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†All b.ps and m.ps are uncorrected. ^1H and ^{31}P NMR spectra were measured on a Bruker WP-60 (F.T.) instrument. Proton chemical shifts are given in ppm downfield from TMS. Phosphorus chemical shifts are given in ppm downfield from an external standard of 85% H_3PO_4. IR spectra were measured on a Perkin–Elmer Model 237 spectrophotometer. Mass spectra were obtained by a Varian MAT CH5 mass spectrometer at 70 eV using a direct inlet system. Microanalyses were carried out by the Hebrew University Microanalytical Laboratory. Gas-chromatographic work was carried out on an F and M Model 720 dual column programmed temperature instrument using a column of 12 ft × 0.25 in. 10% Apiezon L on Diatoport 60–80 at temp. ranging from 90–200°.

[7] W. Wieber and H. U. Werther, *Monatsch. Chem.* **99**, 1153 (1968).

[8] K. D. Bartle, R. S. Edmundson and D. W. Jones, *Tetrahedron* **23**, 1701 (1967).

[9] D. Z. Denney, G. Y. Chen and D. B. Denney, *J. Am. Chem. Soc.* **91**, 6838 (1969).

[10] J. Boutagy and R. Thomas, *Chem. Rev.* **74**, 87 (1974).

[11] M. Schlosser, *Topics in Stereochemistry* (Edited by E. L. Eliel and N. L. Allinger), Vol. 5, pp. 1–30. Wiley, New York (1970).

[12] L. Bergelson and M. M. Shemyakin, *Pure Appl. Chem.* **9**, 271 (1964).

[13] D. H. Wadsworth, O. E. Schupp, E. J. Seus and J. A. Ford, Jr., *J. Org. Chem.* **30**, 680 (1965).

[14] T. H. Kinstle and B. Y. Mandanas, *Chem. Comm.* 1699 (1968).

[15] A. Redjal and J. Seyden-Penne, *Tetrahedron Letters* 1733 (1974).

[16] D. Danion and R. Carrie, *C.R. Acad. Sci. Paris* **269**, 735 (1968).

[17] G. Lefebvre and J. Seyden-Penne, *Chem. Comm.* 1308 (1970).

[18] G. Durrant and J. K. Sutherland, *J. Chem. Soc.* Perkin I, 2582 (1972).

[19] P. Frøyen, *Acta Chem. Scand.* **26**, 2163 (1972).

[20] E. Vedejs and K. A. J. Snoble, *J. Am. Chem. Soc.* **95**, 5778 (1973).

[21] M. Schlosser, A. Piskala, C. Tarchini and Huynh Ba Tuong, *Chimia* **29**, 341 (1975).

[22] F. H. Westheimer, *Accounts Chem. Res.* **1**, 70 (1968).

[23] G. Aksnes and K. Bergesen, *Acta Chem. Scand.* **20**, 2508 (1966).

[24] R. F. Hudson and C. Brown, *Accounts Chem. Res.* **5**, 204 (1972).

[25] P. Gillespie, F. Ramirez, I. Ugi and D. Marquarding, *Angew. Chem.* Internat. edit. **12**, 91 (1973).

[26] T. Koisumi, Y. Watanabe, Y. Yoshida and E. Yoshii, *Tetrahedron Letters* 1075 (1974).

[27] S. Trippett, *Pure Appl. Chem.* **40**, 595 (1974).

[28] M. B. Hocking, *Canad. J. Chem.* **44**, 1581 (1966).

[29] I. F. Wilson and J. C. Tebby, *J. Chem. Soc.* (C), 2713 (1972).

[30] B. Deschamps, J. P. Lampin, I. Matthey and J. Seyden-Penne, *Tetrahedron Letters* 1137 (1977).

[31a] D. Gorenstein and F. H. Westheimer, *J. Am. Chem. Soc.* **92**, 634 (1970); [b] E. A. Dennis and F. H. Westheimer, *Ibid.* **88**, 3432 (1966); [c] P. C. Haake and F. H. Westheimer, *Ibid.* **83**, 1102 (1961).

[32a] D. Gorenstein, *Ibid.* **92**, 644 (1970); [b] G. O. Doak and R. Schmutzler, *Chem. Commun.* 476 (1970); [c] F. Ramirez, *Accounts Chem. Res.* **1**, 168 (1968); [d] D. Houalla, R. Wolf, D. Gagnaire and J. B. Robert, *Chem. Commun.* 443 (1969).

[33] E. L. Muetterties, W. Mahler and R. Schmutzler, *Inorg. Chem.* **2**, 613 (1963).

[34] S. Zbaida and E. Breuer, unpublished work.

[35] For previous applications of phase transfer catalysis to Wittig–Horner reactions see: E. D'Incan and J. Seyden-Penne, *Synthesis* 516 (1975); C. Piechucki, *Ibid.* 187 (1976).

[36] P. Gillespie, P. Hoffmann, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis and I. Ugi, *Angew. Chem.* Internat. Edn **10**, 687 (1971).

[37] S. Trippett, *Phosphor. Sulf.* **1**, 89 (1976).

[38] S. A. Bone, S. Trippett and P. J. Whittle, *J. Chem. Soc.* Perkin I, 80 (1977).

[39] However, compare: B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell and D. W. White, *J. Am. Chem. Soc.* **93**, 4004 (1971).