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THE ALDO-*CIS*-*TRANS*-ENOLIC EQUILIBRIUM OF SUBSTITUTED ALKYL FORMYLACETATES AND ALKYL FORMYLMETHYLPHOSPHONATES

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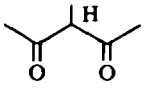
Abstract—A number of substituted ethyl formylacetates and ethyl formylmethylphosphonates were synthesized and their enolization studied by NMR. The ethyl halogen-(or cyan)-formylacetates and formylmethylphosphonates exhibted stable *trans*-enolic forms in solutions. Variation of groupings bonded to the C=O or P=O groups affect the chelating centre basicity. With higher basicity the *cis*-enolic form is stabilized, and *vice versa*. Intermolecular hydrogen bonding stabilizes the *trans*-enolic forms of compounds containing a phosphoryl group.

THE FORMYL GROUP has high enolizing capacity and ranks first in Meyer's enolization series. In the case of β-ketoaldehydes and β-aldoesters, where the keto or ester groups can compete with the formyl groups, enolization is preferably oriented towards the formyl group to form, accordingly, the oxymethylene grouping.

The enolization of β-dicarbonyl compounds can be expected to give stereoisomeric *cis*-(II) and *trans*-(III) enol forms.



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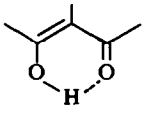

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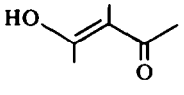


III

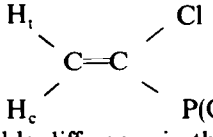
However, no reliable evidence of *trans*-enolization has been found for open chain β-diketones or β-ketoesters.[1,2] At the same time, under certain conditions *trans*-enolization of the formyl group was observed, either along with *cis*-enolization or sometimes even exclusively, in the series of open-chain formyl compounds.[3–9] Thus, Wislicenus obtained crystalline *trans*-enolic forms for alkyl formylphenylacetates.[4] Halogenomalonic dialdehydes exist as *trans*-enols both crystalline and in solutions.[10,11] Malondialdehyde is also a *trans*-enol in water.[12] Yet, in equilibrium solutions of alkyl formylphenylacetate no *trans*-enolic form is found. As the *trans*-enolic form, which when crystalline is stablized by strong intermolecular hydrogen bonds, is dissolved, these bonds are ruptured with consequent transformation of the *trans*-enolic form into more stable aldehyde and *cis*-enolic forms. This transformation is catalysed by acids, and in particular, by the *trans*-enolic form itself.[5] But the *trans*-enolic forms of halogenomalonic dialdehydes are also stable in solutions.

RESULTS AND DISCUSSION

This work is concerned with PMR studies of structural and solvent effects on the enolization of substituted alkyl formylacetates and formylmethylphosphonates: $RCH(CHO)COOC_2H_5$ and $RCH(CHO)P(O)(OC_2H_5)_2$, where R = Cl, Br, CN and i-C_3H_7. Earlier some halide substituted alkyl formylacetates (R = Cl, Br) were described, and their enolization determined by bromometric titration.[13] We have found that certain of these compounds containing a considerable proportion of enol, fail to give a characteristic colour reaction with $FeCl_3$—evidence in favour of *trans*-enolization. PMR spectroscopy confirmed this assumption.

When assigning the proton signals in the PMR spectra characteristic of a single tautomeric form of phosphorus-free compounds, we have relied on earlier PMR-spectroscopic data on alkyl formylphenylacetate.[5] The *trans*-enolic form of this compound is expressed by two intense doublets with chemical shifts 6·57 and 7·84 ppm assigned to the hydroxyl and vinyl protons respectively ($J_{CH—OH}$ = 11·0 Hz). The *cis*-enolic group can be found by a characteristic doublet of the hydroxyl proton engaged in intramolecular hydrogen bonding with chemical shift 12·2 ppm and the corresponding vinyl proton doublet with chemical shift 7·45 ppm ($J_{CH—OH}$ = 13·3 Hz). The aldo-form is characterized by a doublet signal for the formyl group proton at 9·85 ppm and a doublet for the CH proton at 4·62 ppm with $J_{CH—CHO}$ = 3·1 Hz.

The PMR spectra of phosphorus-containing compounds could be expected to give doublet of doublet signals for the vinyl protons of the enolic forms due to hydrogen and phosphorus splitting. Daniewsky, Gordon and Griffin[14] studied the PMR spectra of some α- and β-chlorvinylphosphonates and found two doublet signals for the vinyl protons H_c and H_t with phosphorus coupling constants $J_{P—H_c}$ = 13·6 Hz for the *cis*-proton and $J_{P—H_t}$ = 35·9 Hz for the *trans*-proton in diethyl α-chlorvinyl-



phosphonate These assignments were later confirmed.[15]

The appreciable difference in the vinyl proton spin–spin coupling constants can be applied for identifying the *cis*- and *trans*-enolic forms of substituted alkyl formylmethylphosphonates. It should be noted that the presence, of a *cis*-vinyl proton with a low coupling constant indicates that the hydroxyl-group is *trans* to the phosphoryl group. These substances are treated below as *trans*-enolic forms. Accordingly a substance with a *trans*-vinyl proton (high coupling constant) is a *cis*-enolic form. When assigning signals to particular protons of each form, the integral signal intensities are always taken into account. Naturally, the signals of both protons of the =CHOH group of one and the same form must be equal, whereas the intensities of the =CHOH signals for different forms will depend on the relative amount of each form in solution.

A certain change in chemical shift of the OH-*trans*-form proton observed when the solvent is changed is apparently associated with hydrogen bond formation with the solvent.

The hydroxyl proton of ethyl formylcyanacetate, $NCCH(CHO)COOC_2H_5$, appears as an intense signal (band width >180 Hz) which undoubtedly points to proton exchange. The hydroxyl group proton of diethyl formylcyanmethyl-phosphonate, $NCCH(CHO)P(O)(OC_2H_5)_2$, is represented by only one intense

signal at low field (9·97–12·20 ppm), which corresponds to hydroxyl protons signals of the *cis*- and *trans*-enolic forms averaged by exchange. In polar solvents, as the content of the *trans*-form rises with time, the hydroxyl proton signal is simultaneously somewhat shifted towards higher field.

The PMR data for the compounds studied are given in Table 1.

TABLE 1. THE PMR DATA FOR COMPOUNDS OF THE TYPE $RCH(CHO)COOC_2H_5$ AND $RCH(CHO)P(O)(OC_2H_5)_2$ IN VARIOUS SOLVENTS

Solvents Tautomeric forms; assignments	Chemical shifts in ppm and coupling constants in Hz			
	CCl_4	dioxane	MeCN	$MeNO_2$
1	2	3	4	5
	$ClCH(CHO)COOC_2H_5$			
cis-form				
δ_{CH}	7·31(d)	7·56(d)	—	—
δ_{OH}	11·02(d)	11·16(d)	—	—
$J_{CH—OH}$	15·0	13·3	—	—
trans-form				
δ_{CH}	7·82(bs)	7·89(d)	7·82(d)	7·92(bs)
δ_{OH}	7·24(bs)	8·94(d)	8·14(d)	7·66(bs)
J_{CH-OH}	[a]	12·0	8·6	[a]
aldo-form				
δ_{CH}	4·59(d)	[b]	5·08(d)	5·10(d)
δ_{CHO}	9·36(d)	9·58(d)	9·49(d)	9·58(d)
J_{CH-CHO}	1·3	1·3	1·3	1·3
	$BrCH(CHO)COOC_2H_5$			
cis-form—absent				
trans-form				
δ_{CH}	—	7·59(bs)	8·03(bs)[d]	—
δ_{OH}	—	7·19(bs)	8·03(bs)	—
$J_{CH—OH}$	—	[a]	[a]	—
aldo-form				
δ_{CH}	—	4·91(d)	4·96(d)	—
δ_{CHO}	—	9·22(d)	9·45(d)	—
$J_{CH—CHO}$	—	1·2	1·2	—
	$NCCH(CHO)COOC_2H_5$			
δ_{CH}	—	8·25(s)	8·36(s)	8·46(s)
δ_{OH}	—	10·75(bs)[d]	10·80(bs)[d]	11·15(bs)[d]
J_{CH-OH}	—	[a]	[a]	[a]
trans-form				
δ_{CH}	—	8·05(bs)	8·14(bs)	8·11(bs)
δ_{OH}	—	10·75(bs)[d]	10·80(bs)[d]	11·15(bs)[d]
$J_{CH—OH}$	—	[a]	[a]	[a]
aldo-form—absent				

TABLE 1—*Continued*

Solvents Tautomeric forms: assignments	Chemical shifts in ppm and coupling constants in Hz			
	CCl_4	dioxane	MeCN	$MeNO_2$
1	2	3	4	5
iso-$C_3H_7CH(CHO)COOC_2H_5$				
cis-form				
δ_{CH}	—	—	7·08(d)	—
δ_{OH}	—	—	11·59(d)	—
$J_{CH—OH}$	—	—	13·7	—
trans-form—absent				
aldo-form				
δ_{CH}	—	—	[b]	—
δ_{OH}	—	—	9·65(d)	—
$J_{CH—OH}$	—	—	1·5	—
$C_6H_5CH(CHO)P(O)(OC_2H_5)_2$				
cis-form				
δ_{CH}	7·38(dd)	7·56(dd)	7·47(dd)	7·47(dd)
δ_{OH}	11·32(d)	11·47(d)	11·43(d)[d]	11·44(d)
$J_{CH—OH}$	14·6	14·4	13·4	13·9
$J_{CH—P}$	41·4	41·4	41·4	41·4
trans-form[c]				
δ_{CH}	7·56(dd)	7·65(d)	7·61(d)	7·62(d)
δ_{OH}	11·25(d)	11·14(bs)	11·43(bs)[d]	10·29(bs)
$J_{CH—OH}$	6·7	—	—	—
$J_{CH—P}$	12·0	13·0	12·0	12·0
aldo-form				
δ_{CH}	[b]	[b]	4·49(dd)	[b]
δ_{CHO}	9·74(t)	9·73(t)	9·78(t)	9·84(t)
$J_{CH—CHO}$	2·0	2·0	2·0	2·0
$J_{CH—P}$	—	—	23·4	—
$J_{CHO—P}$	2·0	2·0	2·0	2·0
$ClCH(CHO)P(O)(OC_2H_5)_2$				
cis-form—absent				
trans-form				
δ_{CH}	7·61(d)	7·61(d)	7·65(d)	7·74(d)
δ_{OH}	11·10(bs)	10·13(bs)	9·89(bs)	9·43(bs)
$J_{CH—OH}$	[a]	[a]	[a]	[a]
$J_{CH—P}$	5·3	4·8	8·5	5·9
aldo-form				
δ_{CH}	[b]	[b]	4·98(dd)	4·92(dd)
δ_{CHO}	9·61(t)	9·61(t)	9·65(t)	9·71(t)
$J_{CH—CHO}$	1·0	1·0	1·0	1·0
$J_{CH—P}$	—	—	20·0	20·0
$J_{CHO—P}$	1·0	1·0	1·0	1·0

TABLE 1—*Continued*

Solvents Tautomeric forms: assignments	Chemical shifts in ppm and coupling constants in Hz			
	CCl_4	dioxane	MeCN	$MeNO_2$
1	2	3	4	5
	$BrCH(CHO)P(O)(OC_2H_5)_2$			
cis-form—absent				
trans-form				
δ_{CH}	7·73(d)	7·76(d)	7·69(d)	7·71(d)
δ_{OH}	11·25(bs)	10·18(bs)	9·69(bs)	9·86(bs)
J_{CH-OH}	[a]	[a]	[a]	[a]
J_{CH-P}	6·1	6·5	6·4	6·7
aldo-form				
δ_{CH}	[b]	[b]	4·72(dd)	[b]
δ_{CHO}	9·52(t)	9·44(t)	9·43(t)	9·44(t)
J_{CH-CHO}	1·0	1·0	1·0	1·0
J_{CH-P}	—	--	16·0	—
J_{CHO-P}	1·0	1·0	1·0	1·0
	$NCCH(CHO)P(O)(OC_2H_5)_2$			
cis-form				
δ_{CH}	7·78(d)	7·82(d)	7·96(d)	7·92(d)
δ_{OH}	12·20(bs)[d]	9·97(bs)[d]	10·40(bs)[d]	11·68(bs)[d]
J_{CH-OH}	[a]	[a]	[a]	[a]
J_{CH-P}	35·9	35·3	35·4	35·4
trans-form				
δ_{CH}	7·86(d)	8·10(d)	8·19(d)	7·94(d)
δ_{OH}	12·20(bs)[d]	9·97(bs)[d]	10·40(bs)[d]	11·88(bs)[d]
J_{CH-OH}	[a]	[a]	[a]	[a]
J_{CH-P}	8·0	8·0	8·0	8·0
aldo-form—absent				

s—singlet; bs—broad singlet; d—doublet; dd—doublet of doublets; t—triplet.

[a] spin–spin coupling fails to occur as a result of exchange processes.

[b] the signal is covered by the signals of the solvent, CH_2 or C_6H_5-groups.

[c] the *trans*-form is observed only at the instant of dissolving.

[d] the signal of the CH and OH or OH-*cis*- and *trans*-enolic forms merge into a single signal.

From Table 1 it follows that stable *trans*-enolic forms are present in solutions of halogenated ethyl formylacetates and formylmethylphosphonates.

Equilibrium of the *cis*- and *trans*-enolic forms in solution depends on many factors, notably the formation of hydrogen bonds, steric interactions and enthropy variations.

It is well-known that *cis*-enolic forms are capable of forming intramolecular hydrogen bonds involving a six-membered pseudoaromatic chelate ring. In terms of energy this process is far more advantageous than the formation of intermolecular hydrogen bonding by *trans*-enolic forms. At the same time the closing of the chelate

ring makes the *cis*-enolic forms of β-dicarbonyl compounds less enthropy advantageous than the *trans*-enolic forms (decreased number of degrees of freedom). The high energy of formation of a stable chelate ring in common keto-enols (β-diketones and β-keto-esters with an open chain) compensates this enthropy disadvantage: the *cis–trans* equilibrium determined by free energy differences is totally shifted toward the *cis*-enol.

The factors reducing the stability of intramolecular hydrogen bonding, if they are potent enough, decrease the advantages of the *cis*-enolic form; in such a case a *trans*-enolic form may appear at equilibrium, particularly when strong intermolecular hydrogen bonds are involved, i.e., the crystalline state.

Of these factors one may note steric hindrance and decreased basicity of the hydrogen bond acceptor (the oxygen of the C=O or P=O groups).

Analysis of molecular models of alkyl acetoacetate and acetylacetone and their substituted derivatives reveals that in the α-position the branched substituents create steric interactions opposing the formation of a planar *cis*-enolic form with intramolecular hydrogen bonding. The reason for this phenomenon is overlapping of the α-alkyl and γ-methyl groups. As demonstrated by Rumpf,[16] steric hindrance to enolization arises not only in the *cis*-, but also in the *trans*-enolic form, with the van der Waals radii of the methyl group and the carbonyl oxygen overlapping. The *cis*-enolic chelated forms of non-substituted alkyl acetoacetate and acetylacetone are not hindered sterically, and together with the high energy of intramolecular hydrogen bonding results in exclusive *cis*-enolization. Their homologues with α-branched substituents having steric interactions both in the *cis*- and *trans*-enolic forms are hardly enolizable.[17] The formyl derivatives similar to halogenomalonic dialdehydes or alkyl formylphenylacetates are free from steric hindrance to both *cis*- and *trans*-enolization. This seems to be one of the possible causes of *trans*-enolization in these β-dicarbonyl compounds.

The introduction into the aldoester or dialdehyde molecule of chlorine or bromine atoms whose inductive effect ($\sigma^* = 2{\cdot}8$–$2{\cdot}9$) reduces the basicity of the carbonyl or phosphoryl groups, decreases the energy of intramolecular hydrogen bonding and weakens the pseudoaromatic ring of the *cis*-enolic form. Hence (see above) the decreased content or absence of the *cis*-enolic form in solutions. The phenyl group with its far lower inductive effect ($\sigma^* = 0{\cdot}6$) does not affect the basicity of the C=O or P=O groups to any extent, thus only *cis*- and aldo-forms are present in solution. In this case the *cis*-form forms strong intramolecular hydrogen bonds as evidenced by the high spin–spin coupling constant of the vinyl and hydroxyl protons, $J_{CH-OH} = 12{\cdot}5$ Hz, which is fairly temperature independent. Here the *trans*-form is unstable and, upon dissolving, is transformed into *cis*- and aldo-forms. The cyano-group, along with a pronounced inductive effect ($\sigma^* = 3{\cdot}6$) is also characterized by the conjugation effect ($\sigma_C^- = 0{\cdot}44$) stabilizing the *cis*-chelate ring; in compounds with this grouping, the mixture of *cis*- and *trans*-enolic forms is preserved at equilibrium.

With a view to proving the relationship between the enolization and the effect of the substituent on the basicity of the C=O group, we studied the enolization of β,β,β-trifluorethyl formylphenylacetate, $C_6H_5CH(CHO)COOCH_2CF_3$. Introduction of the CF_3-group lowers the basicity of the chelating centre (C=O group) to which it is bound and partially destabilizes the *cis*-enolic form at equilibrium producing the

trans-enolic form. In such a case (Table 2) as against alkyl formylphenylacetate, we observed at equilibrium in MeCN a *trans*-enolic form together with *cis*- and aldo-forms.

TABLE 2. PMR DATA OF $C_6H_5CH(CHO)COOCH_2CF_3$ IN ACETONITRILE

Assignments	Chemical shifts in ppm and coupling constants in Hz		
	cis-form	*trans*-form	aldo-form
$\delta_{C_6H_5}$	7·31(m)	7·31(m)	7·31(m)
δ_{CH_2}	4·67(q)	4·49(q)	4·64(q)
$J_{CH_2-CF_3}$	8·8	8·8	8·8
δ_{CH}	7·30(d)	7·87(is)[d]	—
δ_{OH}	11·50(d)	7·87(is)[d]	—
J_{CH-OH}	12·0	—	—
δ_{CHO}	—	—	9·62(d)
δ_{CH}	—	—	[b]
J_{CH-CHO}	—	—	1·5

m—multiplet; q —quadruplet; others as Table 1.

Table 1 shows the difference in enolization between ethyl formylchloracetate, $ClCH(CHO)COOC_2H_5$, and diethyl formylchlormethylphosphonate, $ClCH(CHO)P(O)(OC_2H_5)_2$. In the former all three tautomeric forms are present in equilibrium (in CCl_4 and dioxane) in the latter the *cis*-enolic form is not observed in any solvent. The signal with chemical shift 11·1 ppm of the hydroxyl of the enolic form in a CCl_4 solution of formylchlormethylphosphonate corresponds to an associated *trans*-form with intermolecular hydrogen bonding. To prove this, we studied how this signal changed with concentration and found that with progressive dilution the OH signal is gradually shifted toward higher field (at a concentration of 4·8 molar per cent δ = 10·75 ppm, while at 0·8 molar per cent δ = 9·43 ppm). Thus, the substitution of a diethoxyphosphinyl group for a carbethoxy group, leads to a preponderance at equilibrium of a *trans*-enolic form stabilized by intermolecular hydrogen bonding. It is possible that the energy of conjugation in the six-member chelate ring with a P=O group is substantially lower than with a C=O group. For phenyl derivatives, there are no marked differences in enolization between phosphonic and carbonic compounds: both exhibit only *cis*-enolization at equilibrium in all solvents. For diethyl α-formylbenzylphosphonate it was proved by the concentration curve. As distinct from diethyl formylchlormethylphosphonate, the signal of the hydroxyl proton with δ = 11·44 ppm does not change position with a tenfold dilution in $MeNO_2$.

The *trans*-enolic forms of the substituted alkyl formyl acetates differ from the *trans*-enolic forms of the corresponding phosphonates by their susceptibility to association in solutions. Cryoscopic measurements of the former give a normal molecular weight, while in the case of phosphonates it is double or even triple the norm. Table 3 contains the data of cryoscopic and ebullioscopic investigations.

It follows from Table 3 that while the carbonic derivatives are monomers, the phosphonic derivatives are associated in a cryoscopic or ebullioscopic determination in benzene (except diethyl α-formylbenzylphosphonate) but turn into monomers in boiling MeCN where the intermolecular hydrogen bonds are ruptured.

TABLE 3. MOLECULAR WEIGHTS OF SUBSTITUTED ALKYL FORMYLACETATES AND FORMYLMETHYLPHOSPHONATES IN VARIOUS SOLVENTS

Substance	Calc. MW	MW by			
		Cryoscopy		Ebullioscopy	
		C_6H_6	dioxane	C_6H_6	MeCN
$C_6H_5CH(CHO)P(O)(OC_2H_5)_2$[a]	256	—	—	230	240
$ClCH(CHO)COOC_2H_5$	150	156	145	—	—
$ClCH(CHO)P(O)(OC_2H_5)_2$	214	629	—	330	270
$BrCH(CHO)COOC_2H_5$	195	—	195	—	—
$BrCH(CHO)P(O)(OC_2H_5)_2$	295	578	—	—	268
$NCCH(CHO)COOC_2H_5$	141	—	167	—	—
$NCCH(CHO)P(O)(OC_2H_5)_2$	205	—	—	476	218

[a] by isothermic distillation in CCl_4 the molecular weight was found to be 256.[18]

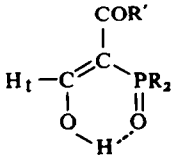
Thus, the intermolecular hydrogen bonding of alkyl formylacetates is not strong and is easily destroyed even when dissolved in benzene, whereas the phosphoryl group, more basic than the carbonyl, ensures strong association of phosphonic derivatives.

The effect of the chelating centre basicity on the enolization is borne out by the example of substituted formylmethylphosphonates which, along with the formyl and P=O groups, also contain a C=O group.

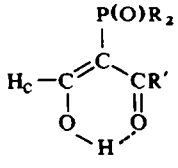
We have synthesized and studied, using PMR spectroscopy, the enolization of the following compounds:

$(C_2H_5O)_2P(O)CH(CHO)COOC_2H_5$, $(C_2H_5O)_2P(O)CH(CHO)COCH_3$, $(C_4H_9)_2P(O)CH(CHO)COOC_2H_5$ and, finally $(C_4H_9)_2P(O)CH(CHO)COCH_3$.

These compounds are capable of forming two enolic forms in which the hydroxyl hydrogen of the oxymethylene group forms a hydrogen bond with the oxygen of the diethoxyphosphinyl or dibuthylphosphinyl groups (Form A), or else with the oxygen of the acetyl or carbethoxy groups (Form B).



Form A



Form B

R = OEt; n-Bu
R′ = OEt; Me.

The signals in the PMR-spectra are assigned to Form A or Form B on the basis of the coupling constants of the vinyl protons (H_c and H_t: see above), as well as by comparison with the spectrum of alkyl formylacetoacetate, $CH_3COCH(CHO)COOC_2H_5$. In the last case the signal of the oxymethylene group hydroxyl proton engaged in intramolecular hydrogen bonding with the acetyl group, is shifted towards lower field (δ_{OH} = 16·91–17·07 ppm in various solvents), as distinct from the signal of the

TABLE 4. THE PMR DATA OF SOME ENOLS WITH INTRAMOLECULAR HYDROGEN BONDING

Tautomeric forms	Chemical shifts in ppm and coupling constants in Hz			
	CCl_4	dioxane	MeCN	$MeNO_2$
1	2	3	4	5
	$CH_3COCH(CHO)COOC_2H_5$			
Chelated form on CH_3CO				
δ_{CH}	9·12(bs)	9·23(bs)	9·18(bs)	9·07(bs)
δ_{OH}	17·07(bs)	17·05(bs)	16·91(bs)	16·98(bs)
$J_{CH—OH}$	[a]	[a]	[a]	[a]
Chelated form on $COOC_2H_5$				
δ_{CH}	9·91(bs)	10·16(bs)	10·07(bs)	9·96(bs)
δ_{OH}	14·41(bs)	14·74(bs)	14·60(bs)	14·58(bs)
$J_{CH—OH}$	[a]	[a]	[a]	[a]
	$(C_2H_5O)_2P(O)CH(CHO)COOC_2H_5$			
Form A				
δ_{CH}	8·24(d)	8·33(d)	8·33(d)	8·30(dd)
$J_{P—H}$	37·8	38·2	39·1	37·8
δ_{OH}	12·80(bs)	12·86(bs)	12·85(bs)	12·86(d)
$J_{CH—OH}$	[a]	[a]	[a]	9·5
Form B				
δ_{CH}	7·84(d)	7·91(d)	7·91(dd)	7·87(dd)
$J_{P—H}$	11·4	8·7	9·0	9·0
δ_{OH}	12·80(bs)	12·86(bs)	12·85(d)	12·86(d)
$J_{CH—O}$	[a]	[a]	12·0	13·1
	$(C_2H_5O)_2P(O)CH(CHO)COCH_3$			
Form A				
δ_{CH}	8·61(d)	8·59(d)	8·59(d)	8·58(d)
$J_{P—H}$	40	40	40	40
δ_{OH}	14·64(bs)[d]	13·51(bs)	13·01(bs)[d]	13·19(bs)
$J_{CH\ OH}$	[a]	[a]	[a]	[a]
Form B				
δ_{CH}	8·54(d)	8·62(d)	8·61(d)	8·25(d)
$J_{CH—P}$	6·4	6·4	6·1	6·7
δ_{OH}	14·64(bs)[d]	15·95(bs)	13·01(bs)[d]	16·51(bs)
$J_{CH—OH}$	[a]	[a]	[a]	[a]

TABLE 4—*Continued*

Tautomeric forms	Chemical shifts in ppm and coupling constants in Hz			
	CCl_4	dioxane	MeCN	$MeNO_2$
1	2	3	4	5
	$(C_4H_9)_2P(O)CH(CHO)COOC_2H_5$			
	in MeCN			
Form A				
δ_{CH_3} in C_4H_9	0·91(t)	δ_{CH_2} in C_4H_9		1·49(m)
δ_{CH_3} in $COOCH_2CH_3$	1·24(t)	δ_{CH_2} in $COOCH_2CH_3$		4·19(q)
δ_{CH}	8·50(d)	δ_{OH}		13·36(bs)
$J_{CH_2-CH_3}$	7·3	J_{CH-P}		23·3
Form B—absent				
	$(C_4H_9)_2P(O)CH(CHO)COCH_3$			
	in MeCN			
Form A				
δ_{CH_3} in C_4H_9	0·86(t)	δ_{CH_2} in C_4H_9		1·47(m)
δ_{CH_3} in $COCH_3$	2·19(s)	δ_{CH}		8·80(d)
δ_{OH}	12·52(bs)	J_{CH-P}		24·0
Form B—absent				

Designations: as Tables 1 and 2.

proton of the oxymethylene group engaged in hydrogen bonding with the carbethoxyl group (δ_{OH} = 14·41–14·74 ppm depending on the particular solvent). The PMR data for the above compounds are given in Table 4.

For diethyl α-formyl-α-acetylmethylphosphonate, $CH_3COCH(CHO)P(O)(OC_2H_5)_2$, in CCl_4, the signal corresponding to the protons of the hydroxyl groups of Forms A and B blend into a single broad signal with a band width at half height of 160 Hz with the centre at 14·64 ppm. Such a marked broading of the spectrum line devoid of a sharply defined peak seems to testify to an equal content of the two forms.

It can be seen from Table 4 that the compounds which, along with the acetyl or carbethoxyl groups, also contain diethoxyphosphinyl groups, are characterized by the presence in equilibrium of Forms A and B. With a more basic dibutylphosphinyl groups there is in equilibrium only one form with a strong intramolecular hydrogen bond (from the oxymethylene group hydroxyl hydrogen to the P=O group). This is yet further proof of the basicity effect of the P=O group on the enolization of the aldo-enols under study.

Comparison of the integral intensities of the signals of each form given in Tables 1, 2 and 4, permits an estimation of the amounts of the forms in solutions. The results are given in Table 5 where the absence of the aldo-form in equilibrium in alkyl formylcyanacetate and formylacetoacetate as well as their phosphorus analogues is shown.

TABLE 5. PERCENTAGE CONTENT OF TAUTOMERIC FORMS IN SOLUTIONS OF SUBSTITUTED ALKYL FORMYLACETATES AND FORMYLMETHYLPHOSPHONATES

	$RCH(CHO)COOC_2H_5$												$RCH(CHO)P(O)(OC_2H_5)_2$											
	CCl_4			dioxane			MeCN			$MeNO_2$			CCl_4			dioxane			MeCN			$MeNO_2$		
	C	T	A	C	T	A	C	T	A	C	T	A	C	T	A	C	T	A	C	T	A	C	T	A
C_6H_5	95[a]	—	5[a]	92		8	90	—	10	85	—	15	95	—	5	93	—	7	89		11	85		15
Cl	10	80	10	16	70	14	—	80	20	-	75	25	—	82	18	—	73	27	—	67	33	—	62	38
Br				—	90	10	—	86	14	—	84	16		70	30	—	57	43	—	50	50	—	45	55
CN				60	40	—	52	48	—	16	84	—	46	54	—	37	63	—	31	69	—	14	86	—
$i\text{-}C_3H_7$	37	—	63[19]	—	—	—	12	—	88															
CH_3CO[b]	67	33		67	33	—	75	25	—															
Form A														50			50			30			20	
Form B														50			50			70			80	
$COOC_2H_5$																								
Form A														81			84			74			73	
Form B														19			16			26			27	

C = *cis*-form; T = *trans*-form; A = aldo-form.

[a] $CDCl_3$.

[b] the first figures refer to the form chelated on the acetyl group, the second —to the form chelated on the carbethoxyl group.

The reason for this is, in all probability, the very high CH-acidity of these compounds. It is known that prototropic equilibria in solution are always shifted towards a less acidic form (in this case the enolic). We have measured the dissociation constants of the compounds investigated in water at 20°C. The results are given in Table 6.

TABLE 6. pK_a VALUES IN WATER FOR SUBSTITUTED ALKYL FORMYLACETATES AND FORMYLMETHYLPHOSPHONATES[b]

Substance	pK_a
$C_6H_5CH(CHO)COOC_2H_5$	7·09[16]
$C_6H_5CH(CHO)P(O)(OC_2H_5)_2$	7·21[16]
$ClCH(CHO)COOC_2H_5$	6·30
$ClCH(CHO)P(O)(OC_2H_5)_2$	6·11
$BrCH(CHO)P(O)(OC_2H_5)_2$	6·14
$NCCH(CHO)COOC_2H_5$	2·04
$NCCH(CHO)P(O)(OC_2H_5)_2$	2·00
$C_2H_5OCOCH(CHO)P(O)(OC_2H_5)_2$	4·09
$CH_3COCH(CHO)P(O)(OC_2H_5)_2$	3·68
$C_2H_5OCOCH(CHO)P(O)(C_4H_9)_2$	6·40[a]

[a] measured in 50 per cent alcohol due to insolubility in water.

[b] although the dissociation constants were measured in an aqueous solution while the contents of the tautomeric forms were determined in organic solvents, one can safely assume that a sharp difference in acidity of two groups of compounds (see Table 6) will also be observed in MeCN or $MeNO_2$ solutions.

Ethyl α-formyl-α-dibutylphosphinylacetate, $(C_4H_9)_2P(O)CH(CHO)COOC_2H_5$, and α-formyl-α-dibutylphosphinylacetone, $(C_4H_9)_2P(O)CH(CHO)COCH_3$, in MeCN contain 100% of Form A.

β,β,β-Trifluorethyl formylphenylacetate, $C_6H_5CH(CHO)COOCH_2CF_3$, in MeCN contains 59% of the *cis*-form, 33% of the *trans*-form and 18% of the aldo-form.

From the data of Table 5, the solvent effect on the enolization may be discussed for four cases: (1) the *trans*-enolic form is absent, with only the *cis*- and aldo-forms showing. Such a situation is observed for the following substances: $C_6H_5CH(CHO)COOC_2H_5$, $i\text{-}C_3H_7CH(CHO)COOC_2H_5$, $C_6H_5CH(CHO)P(O)(OC_2H_5)_2$; polar solvents, in keeping with Meyer's rule, better solvate more polar aldo-form whose proportion increases from CCl_4 and dioxane to MeCN and $MeNO_2$; (2) the aldo-form is absent, with only the *cis*- and *trans*-forms present in equilibrium (substances: $NCCH(CHO)COOC_2H_5$, $NCCH(CHO)P(O)(OC_2H_5)_2$; the *trans*-form is a more polar form, its content increases with the polarity of the solvent; (3) the *cis*-form is absent, with only the *trans*- and aldo-forms present in equilibrium—observed in the case of $ClCH(CHO)COOC_2H_5$ in polar solvents and $BrCH(CHO)COOC_2H_5$ and $ClCH(CHO)P(O)(OC_2H_5)_2$, $BrCH(CHO)P(O)(OC_2H_5)_2$. Since experimental data suggest that the aldo-form content increases with solvent polarity, obviously it is the more polar of the two forms; (4) the aldo-form is absent, present in equilibrium are two *cis*-enolic forms with intramolecular hydrogen bonds

with the C=O or P=O groups: $CH_3COCH(CHO)COOC_2H_5$, $C_2H_5OCOCH(CHO)P(O)(OC_2H_5)_2$, $CH_3COCH(CHO)P(O)(OC_2H_5)_2$, $(C_4H_9)_2P(O)CH(CHO)COOC_2H_5$ and $(C_4H_9)_2P(O)CH(CHO)COCH_3$; the ratio of these forms depends mainly on the acceptor properties of the acetyl, carbethoxyl, diethoxy- and dibutylphosphinyl groups with respect to the oxymethylene group proton; as the polarity of the solvent rises, so does the content of the B form.

EXPERIMENTAL

The substituted alkyl formylacetates were prepared as described in the literature. When synthesizing β,β,β-trifluorethyl formylphenylacetate, $C_6H_5CH(CHO)COOCH_2CF_3$, from trifluorethyl phenylacetate, ethyl formate could not be used for formylation as it caused transesterification to form alkyl formylacetate. Formylation was carried out using trifluorethyl formate, $HCOOCH_2CF_3$, prepared in dibutyl ether in the presence of NaH.

The substituted alkyl formylmethylphosphonates were obtained either by ethyl formate formylation of the appropriate substituted methyl phosphonates, or by transforming them into ethoxymethylene derivatives using ethyl orthoformate in the presence of Ac_2O followed by the hydrolysis.

In order to synthesize formyldibutylphosphinylacetone, $(C_4H_9)_2P(O)CH(CHO)COCH_3$, dibutylmethylphosphinoxide was metallized with BuLi; the subsequent reaction with EtOAc yielded dibutylphosphinylacetone, $(C_4H_9)_2P(O)CH_2COCH_3$, which was converted into dibutylphosphinyl(ethoxymethylene)acetone, $(C_4H_9)_2P(O)C(=CHOC_2H_5)COCH_3$, and further subjected to hydrolysis.

Ethyl formylchloracetate, $ClCH(CHO)COOC_2H_5$. Obtained by formylation of ethyl chloracetate;[18] yield 45%, m.p. 83–84° (from benzene). (Found: C, 40·0, 39·9; H, 4·9, 4·9; Cl, 22·9, 23·0. Calc. for $C_5H_7ClO_3$: C, 39·9; H, 4·7; Cl, 23·6%). No colour reaction with $FeCl_3$. Lit.[20] m.p. 85°.

Ethyl formylbromacetate, $BrCH(CHO)COOC_2H_5$. Obtained by formylation of ethyl bromacetate;[21] yield 26%, m.p. 84–85°. (Found: C, 30·8, 31·0; H, 3·5, 3·7; Br, 41·8, 41·4. Calc. for $C_5H_7BrO_3$: C, 30·8; H, 3·6; Br, 41·0%). No colour reaction with $FeCl_3$. Lit.[21] m.p. 83–84°.

Ethylformylcyanacetate, $NCCH(CHO)COOC_2H_5$. Obtained from ethyl cyanacetate using ethyl orthoformate and Ac_2O followed by hydrolysis of the ethoxymethylene derivative,[22] $NCC(=CHOC_2H_5)COOC_2H_5$. Yield 52%, m.p. 67–68°. Strong orange colour with $FeCl_3$. Lit.[22] m.p. 69°.

Ethyl formylisovalerate, $i\text{-}C_3H_7CH(CHO)COOC_2H_5$. Obtained by the Reformatsky reaction (as described)[23] from ethyl bromisovalerate and ethyl orthoformate in the presence of Zn followed by hydrolysis of the acetal obtained. Yield: 10%. Purified by prep. chromatograph. B.p. 72–73°/10 mm; semicarbazone: m.p. 108–109°. Lit.[23] b.p. 68–70/9 mm; semicarbazone: m.p. 108°.

β,β,β-trifluorethyl phenylacetate, $C_6H_5CH_2COOCH_2CF_3$. A mixture of 15·5 g (0·1 mole) of phenacylchloride and 10 g (0·1 mole) of trifluorethanol was refluxed for 2 hr. Vacuum distillation yielded 19·8 g (89%) of β,β,β-trifluorethyl phenylacetate with b.p. 92°/10 mm, n_D^{20} 1·4470, d_4^{20} 1·2418. (Found: C, 54·9, 55·1; H, 4·2, 4·3; F, 26·0, 26·4. Calc. for $C_{10}H_9O_2F_3$: C, 55·1; H, 4·1; F, 26·2%).

Trifluorethyl formate. A mixture of 31 g (0·3 mole) of trifluorethanol, 18 g (0·31 mole) of 8% HCOOH and 2·7 g of $CaCl_2$ was slowly heated on a water bath in a flask with a 25-cm high fractionating column, when trifluorethyl formate gradually distilled. 30 g of a fraction with b.p. 40–50° was obtained and redistilled over P_2O_5 to yield 22 g (44%) of ester with b.p. 43–44°, n_D^{20} 1·3025, d_4^{20} 1·3448. (Found: C, 28·2; 28·4; H, 2·7, 2·8; F, 44·3, 44·6; MR_D 17·81. Calc. for $C_3H_3F_3O_2$: C, 28·2; H, 2·3; F, 44·5%; MR_D 17·83).

β,β,β-Trifluorethyl formylphenylacetate, $C_6H_5CH(CHO)COOCH_2CF_3$. A mixture of 8·7 g (0·04 mole) of trifluorethyl phenylacetate and 5·2 g (0·04 mole) trifluorethyl formate was added to a suspension of 5 g (0·21 mole) of NaH in 30 ml of absolute dibutyl ether, boiled for 6 hr and left for 12 hr. The precipitate was filtered, washed with absolute ether and treated by 30 ml of 10% H_2SO_4. The oil obtained was extracted with $CHCl_3$ and dried ($MgSO_4$). 4·5 g (46%) of a substance was obtained with b.p. 76–77°/1·5 mm, n_D^{20} 1·4892, d_4^{20} 1·3084. (Found: C, 53·2, 53·5; H, 3·7, 3·8; F, 22·9, 23·2. Calc. for $C_{11}H_9O_3P_3$: C, 53·6; H, 3·7; F, 23·2%). Gives a purple colour with alcoholic $FeCl_3$.

Ethyl formylacetoacetate, $CH_3COCH(CHO)COOC_2H_5$. Obtained by the method described.[24] Yield 60%; b.p. 92–96°/23 mm, n_D^{20} 1·4710, d_4^{20} 1·1342. Lit.[24] b.p. 95°/21 mm.

Diethyl formylchlormethylphosphonate, $ClCH(CHO)P(O)(OC_2H_5)_2$. A mixture of 10 g (0·054 mole) of diethyl chlormethylphosphonate[25] and 4 g (0·054 mole) of ethyl formate was added to a suspension of 1·23 g (0·054 g-atom) of Na in ether (50 ml). After 24 hr the mixture was diluted with water (150 ml) until the

precipitate completely dissolved. The organic layer was separated, the water layer twice washed with $CHCl_3$, acidified (Congo Red indicator) with H_2SO_4 and extracted with $CHCl_3$. 6·5 g of a substance was obtained with b.p. 90–91°/1·5 mm; yield 57%. It was recrystallized from a mixture of ether and petroleum ether; m.p. 61·5–63°. (Found: C, 33·5, 33·4; H, 5·6, 5·6; Cl, 16·8, 17·0; P, 14·7, 14·8. Calc. for $C_6H_{12}O_4ClP$: C, 33·6; H, 5·6; Cl, 16·5; P, 14·4%). Dinitrophenylhydrazone: m.p. 138–139° (from alcohol). (Found: N, 15·6, 15·5. Calc. for $C_{12}H_{16}N_4O_7Cl$: N, 15·4%). Does not give a colour reaction with $FeCl_3$.

Diethyl formylbrommethylphosphonate. $BrCH(CHO)P(O)(OC_2H_5)_2$. A mixture of 10·3 g (0·045 mole) of diethyl brommethylphosphonate[26] and 3·3 g (0·045 mole) of ethyl formate was added to a suspension of 1·03 g (0·045 mole) of Na in ether (50 ml). The mixture was heated for 1 hr to 35° and left for 24 hr following which it was diluted with water (150 ml). The organic layer was separated, the water layer washed with $CHCl_3$, acidified with H_2SO_4 and extracted with $CHCl_3$. After drying (Na_2SO_4) and distillation, a fraction was obtained b.p. 100–110°/1 mm which solidified. Following crystallization (ether/pentane) 4·9 g (yield 42%) of a substance with m.p. 76–78° was obtained. (Found: C, 27·8, 27·7; H, 4·6, 4·6; P, 12·1, 12·1; Br, 31·2, 30·9. Calc. for $C_6H_{12}O_4BrP$: C, 27·8; H, 4·6; P, 12·0; Br, 30·8%). Dinitrophenylhydrazone: m.p. 145–146° (from alcohol). (Found: N, 13·6, 13·8. Calc. for $C_{12}H_{16}N_4O_7Br$: N, 13·7%). No colour reaction with $FeCl_3$.

Diethyl ethoxymethylencyanmethylphosphonate. $(C_2H_5O)_2P(O)C(=CHOC_2H_5)CN$. A mixture of 15·5 g (0·087 mole) of diethyl cyanmethylphosphonate,[27] 13 g (0·087 mole) of ethyl orthoformate and 18·2 g (0·176 mole) of Ac_2O was refluxed for 6 hr; the light fractions were distilled at a bath temperature of 200°; the residue was vacuum fractionated to yield 10 g of intial diethyl cyanmethylphosphonate with b.p. 132–134°/6 mm, n_D^{20} 1·4340, and 1·7 g (24%) (calculated in terms of the reacting substance) of a substance with b.p. 160–162°/0·1 mm, n_D^{20} 1·4661, d_4^{20} 1·1182. (Found: C, 46·4, 46·2; H, 7·0, 6·9; P, 12·6, 12·7. Calc. for $C_9H_{16}O_4PN$: C, 46·4; H, 6·9; P, 13·3%).

Diethylformylcyanmethylphosphonate. $(C_2H_5O)_2P(O)CH(CHO)CN$. 1·7 g of diethyl ethoxymethylencyanmethylphosphonate was dissolved in 1·5% NaOH aq (20 ml). The solution was acidified with cooled 15% H_2SO_4 (Congo Red indicator) and extracted with $CHCl_3$. After drying Na_2SO_4, the extract yielded a fraction with b.p. 122–124°/2 mm which crystallized after distillation. 0·4 g (27%) of a substance was obtained with m.p. 58–60° (benzene–hexane). (Found: C, 41·4, 41·1; H, 5·9, 5·8; P, 15·1, 15·0. Calc. for $C_7H_{12}O_4PN$: C, 41·0; H, 5·9; P, 15·1%). Dinitrophenylhydrazone: m.p. 90–92° (EtOH). (Found: N, 17·8, 17·8. Calc. for $C_{13}H_{17}O_7PN_5$: N, 18·2%). Lit.[27] b.p. 94–97°/1 mm, n_D^{20} 1·4725, d_4^{20} 1·1836. Gives a strong orange-red colour with $FeCl_3$.

Diethyl α-formyl-α-carbethoxymethylphosphonate, $C_2H_5OCOCH(CHO)P(O)(OC_2H_5)_2$. A mixture of 10 g (0·045 mole) of diethyl α-carbethoxymethylphosphonate, 3·3 g (0·045 mole) of ethyl formate and 2·5 ml of abs EtOH was added to a suspension of 1·03 g (0·045 g-atom) of Na in absolute ether (40 ml) at 0°, maintaining gentle reflux. The mixture was left for 24 hr at ambient temp, then water (150 ml) was added and the organic layer separated. The water layer was extracted with $CHCl_3$, dried (Na_2SO_4) and distilled giving an oil, 3 g, (26%) b.p. 93–94°/1 mm, n_D^{20} 1·4515, d_4^{20} 1·1670. (Found: C, 42·7, 42·8; H, 6·9, 6·9; P, 12·2, 12·1. Calc. for $C_9H_{17}O_6P$: C, 42·9; H, 6·8; P, 12·3%). Dinitrophenylhydrazone: m.p. 146–148°. Lit.[28] b.p. 130–135°/2·5 mm, dinitrophenylhydrazone m.p. 146–148°. Gives a bright-orange colour with $FeCl_3$.

Diethyl α-acetyl-α-ethoxymethylenmethylphosphonate, $CH_3COC(=CHOC_2H_5)P(O)(OC_2H_5)_2$. A mixture of 29·4 g (0·151 mole) of diethyl acetomethylphosphonate,[29] 30·4 g (0·30 mole) of Ac_2O and 16 g (0·151 mole) of ethyl orthoformate was refluxed for 6 hr, the light fractions were distilled at a bath temperature of 200°. The residue was vacuum fractionated to yield 14 g of the initial diethyl acetomethylphosphonate and 11·2 g (32%) of a substance with b.p. 104–105°/0·4 mm, n_D^{20} 1·4710, d_4^{20} 1·1210. (Found: C, 48·2, 48·0; H, 7·7, 7·7; P, 12·6, 12·7. Calc. for $C_{10}H_{19}O_5P$: C, 48·0; H, 7·7; P, 12·4%).

Diethyl α-formyl-α-acetylmethylphosphonate, $CH_3COCH(CHO)P(O)(OC_2H_5)_2$. 6·1 g (0·024 mole) of diethyl α-acetyl-α-ethoxymethylenmethylphosphonate was dissolved in 2·5% NaOH aq (20 ml). The solution obtained was acidified with dil. H_2SO_4 and extracted with $CHCl_3$. The extract yielded 4 g (74%) of a substance with b.p. 89·5–90°/1·5 mm, n_D^{20} 1·4630, d_4^{20} 1·1712. (Found: C, 43·3, 43·1; H, 7·0, 7·0; P, 13·8, 13·8, neutralization equivalent 220·8. Calc. for $C_8H_{15}O_5P$: C, 43·2; H, 6·8; P, 14·0%, neutralization equivalent 222·2). Gives a bright-orange colour with $FeCl_3$. Cupric salt, recrystallized from alcohol–hexane m.p. 221–222° (dec.). (Found: C, 37·6, 37·5; H, 5·5, 5·6; P, 11·8, 11·9; Cu, 12·5, 12·6. Calc. for $(C_8H_{14}O_5P)_2Cu$: C, 38·0; H, 5·5; Cu, 12·6%).

Diethyl α-formyl-α-dibutylphosphinylacetate, $(C_4H_9)_2P(O)CH(CHO)COOC_2H_5$. A mixture of 10 g (0·044 mole) of diethyl dibutylphosphinylacetate, b.p. 141–145°/2 mm, n_D^{20} 1·4625, m.p. 30°, and 2·96 g (0·044 mole) of ethyl formate was added to a suspension of 1 g (0·044 g-atom) of Na in absolute ether (30 ml) at 0°. The mixture was boiled for 30 min, stirred for 5 hr at ambient temp and left for 12 hr. The precipitate

was dissolved in water (20 ml); the water layer washed with ether, acidified with conc. H_2SO_4 and extracted with $CHCl_3$. Drying ($MgSO_4$) and vacuum distillation 6 g (55%) gave a substance with b.p. 106–107°/0·02 mm, n_D^{20} 1·4737, d_4^{20} 1·0338. (Found: C, 56·5, 56·6; H, 9·2, 9·2; P, 11·2, 11·5. Calc. for $C_{13}H_{25}PO_4$: C, 56·5; H, 9·1; P, 11·2%). Gives an orange colour with $FeCl_3$.

Dibutyl phosphinylacetone, $(C_4H_9)_2P(O)CH_2COCH_3$. A solution of BuLi (prepared from 25·3 g (0·18 mole) of BuBr and 5 g of Li in 150 ml of absolute ether was added to a solution of 25 g (0·15 mole) of dibutylmethylphosphinoxide in 150 ml of absolute ether at −5°. The mixture was refluxed for 4 hr, cooled to ambient temp, and 26 g (0·3 mole) of absolute EtOAc added. The mixture was refluxed for 12 hr, water added (100 ml) and the organic layer separated. The water layer was extracted with $CHCl_3$, the extract dried ($MgSO_4$) and distilled to give 10 g (30%) of dibutylphosphinylacetone, b.p. 103–104°/0·5 mm, m.p. 46·5–48·5°. (Found: C, 61·1, 60·8; H, 10·6, 10·6; P, 14·4, 14·1. Calc. for $C_{11}H_{23}PO_2$: C, 60·6; H, 10·6; P, 14·2%).

Dibutylphosphinyl(ethoxymethylen)acetone, $(C_4H_9)_2P(O)C(=CHOC_2H_5)COCH_3$. A mixture of 10 g (0·046 mole) of dibutylphosphinylacetone, 9·4 g (0·092 mole) of Ac_2O and 6·8 g (0·046 mole) of ethyl orthoformate was refluxed for 12 hr and distilled at a bath temp of 200°. The residue was vacuum fractionated to yield 4 g of the initial substance and 4 g (53% in terms of the reacting product) of a substance with b.p. 136–137°/0·5 mm, n_D^{20} 1·4745, d_4^{20} 0·9912. (Found: C, 61·3, 61·3; H, 10·0, 10·0; P, 11·9, 12·0. Calc. for $C_{14}H_{27}PO_3$: C, 61·3; H, 9·9; P, 11·3%).

Formyl(dibutylphosphinyl)acetone, $(C_4H_9)_2P(O)CH(CHO)COCH_3$. 2 g (0·004 mole) of dibutylphosphinyl(ethoxymethylen)acetone was dissolved in 10 ml of 2·5% NaOH aq (10 ml). The solution was acidified with dil H_2SO_4 and extracted with $CHCl_3$. Following drying and vacuum distillation 1·1 g (61%) of a substance was obtained with b.p. 106–107°/0·5 mm, n_D^{20} 1·4844, d_4^{20} 1·0192. (Found: C, 58·9, 58·9; H, 9·7, 9·7; P, 12·9, 13·0. Calc. for $C_{12}H_{23}PO_3$: C, 58·5; H, 9·4; P, 12·6%). Gives a bright-orange colour with $FeCl_3$.

All synthesized substances showed one spot on TLC on silica gel, 10% deactivated (3:2 hexane–acetone system). The PMR-spectra were taken on Perkin–Elmer R-12 and Hitachi–Perkin–Elmer R-20 spectrometers (60 MHz) having hexamethyldisiloxane as internal standard. The chemical shifts were measured on the δ-scale.

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