693. *The Synthesis of Acetylenes and Allenes from Enol Phosphates.*[1]

By J. CYMERMAN CRAIG and M. MOYLE.

Enol phosphates, $R' \cdot CH:CR \cdot O \cdot PO(OEt)_2$, readily obtainable from largely or slightly enolised ketones, are smoothly converted into the mono- or di-substituted acetylenes on treatment with sodamide in liquid ammonia. Both *trans*- and *cis*-enol phosphates undergo the elimination, and the reaction requires the presence of a double bond in the group R' in conjugation with the olefinic linkage in the enol or, when R' = H, in the group R. If the enol phosphate contains a methylene group adjacent to the central carbon–carbon double bond, allenes are produced, and terminal acetylenes may be trans-formed into monosubstituted diacetylenes, no activation other than the original triple bond being required. The reactions support the suggested biosynthetic pathway involving enol phosphates.

THE number of naturally occurring acetylenic compounds [2] exceeds 150 though only a small fraction of the plant kingdom has been explored so far. However, whereas the role of acetate as a precursor for the biogenesis of fatty acids, terpenes, and steroids is well established, with the intermediary formation of acetoacetyl coenzyme A, mevalonic acid, and isopentenyl pyrophosphate, detailed knowledge of the biosynthesis of the triple bond is lacking. Recent evidence [3] supports the genesis of the acetylenic linkage from acetate units. In view of the high energy required for the direct dehydration of $CO \cdot CH_2$ to $C:C$ groups this conversion could be expected to occur more easily in two steps, through an enol ester $C(OX):CH$ which can eliminate an anionic leaving group with prior or simultaneous loss of a proton from the *trans*-position of the double bond. The phosphate [2a] and the pyrophosphate [4] anions have been suggested as leaving groups in Nature. The reverse reaction, that of addition of water to the triple bond, is well known *in vitro* and also occurs biologically,[5] as demonstrated by the discovery of an organism converting acetylene-

[1] For a preliminary communication see *Proc. Chem. Soc.*, 1962, 149.
[2] (a) Bohlmann and Mannhardt, *Progr. Chem. Org. Nat. Prod.*, 1957, **14**, 1; (b) Jones, *Proc. Chem. Soc.*, 1960, 199; (c) Sörensen, *ibid.*, 1961, 98.
[3] Bu'lock and Gregory, *Biochem. J.*, 1959, **72**, 322; Bu'lock, Allport, and Turner, *J.*, 1961, 1654.
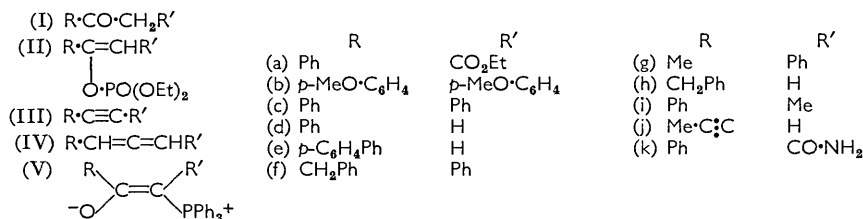[4] Jones, *Chem. Eng. News*, 1961, **39**, No. 12, 46.
[5] Eimhjellen, *Acta. Chem. Scand.*, 1956, **10**, 1049.

dicarboxylic acid (its sole carbon source) into oxaloacetic acid. The usual reversibility of enzymic reactions suggests that the dehydration of β-keto-acids to acetylenes should also occur under relatively mild conditions. The conversion of enol phosphates into acetylenes as model for acetylene biosynthesis was therefore investigated. The only recorded transformation of an enol phosphate into an acetylene appears to be the formation [6] of diethyl propynephosphonate by the action of sodium ethoxide on 1-(diethyl phosphatoisopropenyl) diethyl phosphate.

Vinyl phosphates [7] may be obtained from enolisable ketones by reaction of the sodium enolate with a phosphoryl chloride; this reaction yields the *trans*-isomers exclusively (*cis* and *trans* refer, as usual, to the carbon chain; for the enol phosphates discussed here they thus define also the H/PO(OR)$_2$ relation). Thus, ethyl benzoylacetate with diethyl phosphorochloridate gave diethyl *trans*-2-ethoxycarbonyl-1-phenylvinyl phosphate (IIa) and with diphenyl phosphorochloridate afforded the corresponding diphenyl *trans*-ester. In the same way, the use of diethyl phosphorochloridate gave diethyl *trans*-1,2-di-*p*-methoxyphenylvinyl phosphate (IIb) from deoxyanisoin. With ketones that enolise little or not at all the interaction of the α-chloro-ketone with triethyl phosphite by the Perkow reaction [7,8] yields predominantly the *cis*-enol phosphate. In this way phenylacetone, through 1-chloro-1-phenylacetone, gave diethyl *cis*-α-methylstyryl phosphate (IIg); dibenzyl ketone, through 1-chloro-1,3-diphenylacetone, yielded diethyl *cis*-α-benzylstyryl phosphate (IIf); and propiophenone, through 2-chloro-1-phenylpropan-1-one, afforded diethyl *cis*-1-phenylpropenyl phosphate (IIi).

The Perkow reaction may also be used to obtain *cis*-enol phosphates from enolisable ketones. Ethyl α-chlorobenzoylacetate yielded diethyl *cis*-2-ethoxycarbonyl-1-phenylvinyl phosphate (IIa), and deoxybenzoin, through the α-chloro-compound, afforded diethyl *cis*-α-phenylstyryl phosphate (IIc). Finally, methyl ketones are transformed, through their chloromethyl derivatives, into vinyl phosphates containing a terminal methylene group: for instance, phenacyl chloride and 4-phenylphenacyl chloride gave diethyl 1-phenylvinyl phosphate (IId) and diethyl 1-(4-biphenylyl)vinyl phosphate (IIe), and benzyl chloromethyl ketone afforded diethyl 1-benzylvinyl phosphate (IIh).

(I) R·CO·CH$_2$R′
(II) R·C=CHR′
    |
    O·PO(OEt)$_2$
(III) R·C≡C·R′
(IV) R·CH=C=CHR′
(V) R, R′, C=C, $^-$O, PPh$_3^+$

	R	R′		R	R′
(a)	Ph	CO$_2$Et	(g)	Me	Ph
(b)	*p*-MeO·C$_6$H$_4$	*p*-MeO·C$_6$H$_4$	(h)	CH$_2$Ph	H
(c)	Ph	Ph	(i)	Ph	Me
(d)	Ph	H	(j)	Me·C⋮C	H
(e)	*p*-C$_6$H$_4$Ph	H	(k)	Ph	CO·NH$_2$
(f)	CH$_2$Ph	Ph			

Reaction of dilute aqueous sodium hydroxide on the *trans*-enol phosphate (IIa) in 50% aqueous dioxan or 50% aqueous alcohol at 5° or at 25° gave only acetophenone. The absence of recovered enol phosphate indicated that displacement of phosphate by hydroxyl ion had occurred, accompanied by hydrolysis of the carboxylic ester and decarboxylation of the β-keto-acid so formed. Using potassium hydroxide in refluxing absolute ethanol gave up to 20% of phenylpropiolic acid, with much acetophenone. The findings that elimination was retarded by aqueous media and accelerated by using an alcoholic solution and a stronger base (ethoxide) suggested the characteristics of an $E2$ elimination in which, owing to the greater charge-dispersal in the $E2$ transition state the $E2$ rate changes faster than the S_N2 rate with decreasing ion-solvating power of the medium.[9]

[6] Jacobson, Griffin, Preis, and Jensen, *J. Amer. Chem. Soc.*, 1957, **79**, 2600.
[7] Lichtenthaler, *Chem. Rev.*, 1961, **61**, 607.
[8] Perkow, Ullerich, and Meyer, *Naturwiss.*, 1952, **39**, 353.
[9] Cooper, Dhar, Hughes, Ingold, MacNulty, and Woolf, *J.*, 1948, 2043; Hine, "Physical Organic Chemistry," 2nd edn., McGraw-Hill Book Co., Inc., New York, 1962, p. 205.

Accordingly, the use of sodamide in liquid ammonia at —70° gave phenylpropiolamide smoothly in 72% yield. In agreement with the greater base strength of amide ion than of hydroxyl ion, the absence of acetophenone or of β-keto-ester from the product showed that the competing substitution had been suppressed under these conditions. At —33° phenylacetylene was the sole product (75%), owing to a fission [10] which formally resembles the Haller–Bauer [11] cleavage of non-enolisable ketones by sodamide and will be reported in detail later.

Identical results were obtained when diphenyl *trans*-2-ethoxycarbonyl-1-phenylvinyl phosphate was used (see Table). Since this work was completed, publications by Nakaminami and his colleagues [12] have appeared, in which diphenyl *trans*-2-methoxy-carbonyl-1-phenylvinyl phosphate was prepared and found to give phenylacetylene (28%) by action of sodamide in liquid ammonia. They achieved base-induced elimination from enol esters, giving αβ-acetylenic carbonyl compounds by the use of sodium t-butoxide in benzene.

The *cis*-enol phosphate (IIa), subjected to the previously used conditions (sodamide in liquid ammonia at —33°), gave phenylacetylene in almost the same (65%) yield as the *trans*-isomer, and free from ketone or ester. At —70° most (80%) of the enol phosphate was recovered, with 12% (spectroscopic) of phenylpropiolamide. The formation of phenylpropiolamide is in agreement with the known greater ease of conversion of esters into amides in αβ-acetylenic than in αβ-ethylenic systems. For instance, ethyl phenyl-propiolate affords phenylpropiolamide with liquid ammonia alone, while both ethyl cinnamate and diethyl 2-ethoxycarbonyl-1-phenylvinyl phosphate (IIa) are unchanged by this reagent. It is evident that the speed of elimination of the *trans*-enol phosphate (IIa) at —70° is appreciably faster than that of its *cis*-isomer, and that, if the *cis*-enol phosphate had under the conditions of this experiment (—70°) suffered isomerisation to the *trans*-isomer, then the whole system would have undergone elimination. That this was not the case was shown by the recovery of 80% of the *cis*-enol phosphate.

It is well known that base-promoted *trans*-elimination is fast because the atoms concerned lie in a coplanar arrangement in which the dihedral angle between hydrogen and the departing anion is 180°. However, in the *cis*-enol phosphate (IIa) in which the dihedral angle is 0°, the transition state is still flat and coplanar, and a coplanar *cis*-elimination should thus readily take place. It was recently reported [13] that *trans*-2-phenylcyclo-pentyl toluene-*p*-sulphonate and its *cis*-isomer both underwent base-promoted E_2 elimin-ation, with a ratio *k*-trans : *k*-cis of only 14 : 1, while the corresponding 2-phenylcyclohexyl ester had *k*-trans : *k*-cis > 10^4 : 1 and the reason advanced was that the small dihedral angle in the *cis*-cyclopentyl system (*ca.* 12°) approaches coplanarity whereas this would not be the case for the *cis*-cyclohexyl compounds in which the dihedral angle will remain at 60°.

In our cases, the ratio *k*-trans : *k*-cis is at least 6 : 1, and *cis*- and *trans*-coplanar elimin-ations both appear relatively easy. In agreement, the *trans*-enol phosphate (IIb) from deoxyanisoin, and the *cis*-enol phosphate (IIc) from deoxybenzoin, both gave the expected diphenylacetylenes in >90% yield.

An enol phosphate derived from a chloromethyl ketone exists as only one isomer and undergoes similar ready elimination to give the terminal acetylene. For instance, the enol phosphates (IId and e) gave phenyl- and 4-diphenylyl-acetylene, respectively, in high yield. When the enol phosphate contained a methylene group adjacent to the carbon–carbon double bond, allenic products were obtained: the *cis*-enol phosphate (IIf) afforded 1,3-diphenylallene (IVc), and phenylallene (IVd) in good yield was obtained from both the similarly constituted enol phosphates (IIh and g). Base-catalysed rearrangement of

[10] Craig and Moyle, *Proc. Chem. Soc.*, 1962, 283.
[11] Haller and Bauer, *Compt. rend.*, 1908, **147**, 824; Hamlin and Weston, *Org. Reactions*, 1957, 9, 1.
[12] Nakagawa, Nakaminami, Ogura, and Ono, *Bull. Chem. Soc. Japan*, 1962, **35**, 1485, 1488; Nakaminami, *ibid.*, 1962, **35**, 1629.
[13] DePuy, Thurn, and Morris, *J. Amer. Chem. Soc.*, 1962, **84**, 1314.

1,3-diphenylpropyne and of 1-phenylpropyne to the corresponding allenes is well known [14] and formation of allenes in this system is therefore to be expected.

In all cases so far discussed, the group R' contains a double bond in conjugation with the olefinic carbon–carbon linkage of the enol phosphate (II), or, when R' = H, the group R contains a double bond similarly situated.

The *cis*-enol phosphate (IIi) from propiophenone gave neither acetylene nor allene. No enol phosphate was recovered, and the infrared spectrum showed only aromatic-ketone absorption. Similarly, the enol phosphate (II; R = n-$C_{13}H_{27}$, R' = H) from 1-chloro-pentadecan-2-one gave no acetylene or allene, only pentadecan-2-one being obtained. Clearly, in the last two cases, owing to the reduced acidity of the olefinic hydrogen atom in the enol phosphate, only the competing substitution had occurred, resulting in hydrolysis to the parent ketone. Acetylenes or allenes can thus be obtained from enol phosphates only if the conditions outlined above are fulfilled.

The *cis*-enol phosphate (IIg) gave phenylallene (IVd) in high yield, showing that when R' contains a double bond in conjugation with the olefinic carbon–carbon linkage of the enol phosphate the presence of a similar linkage in the group R is not necessary for an elimination.

The conversion of the enol phosphate (IIh) into phenylallene (IVd) may be due to abstraction of a proton from the doubly activated methylene group in (IIh), to be discussed in a forthcoming publication. Acetylenic acids have recently been synthesised by the action of alkali on the enol arenesulphonates from certain disubstituted diethyl malonates; [15] and, in addition to the activation provided by the ester group, the presence of an unsaturated linkage in conjugation with the enol carbon–carbon double bond is necessary for this reaction. A recent synthesis of disubstituted acetylenes [16] by pyrolysis of β-oxoalkylidenetriphenylphosphoranes (V) similarly required that either R or R' was a phenyl or carbonyl group or the equivalent. These phosphoranes are analogous to the *cis*-enol phosphates reported here. Reaction of chloroacetyl chloride with sodio-propyne gave 1-chloropent-3-yn-2-one which formed the enol phosphate (IIj) on reaction with triethyl phosphite. This acetylenic enol phosphate underwent elimination smoothly, to give penta-1,3-diyne (IIIj), isolated as the condensation product [17] with benzaldehyde. The method is thus applicable to the transformation of any terminal acetylene into a monosubstituted diacetylene and can be extended further since no activation other than the triple bond in the original acetylene appears necessary. Attempted synthesis of diacetylenic carboxylic acids by the enol arenesulphonate method gave [18] only tetronic acids by intramolecular cyclisation. All enol phosphates (II) show characteristic infrared absorption maxima in the 6·0 μ region, due to the C=C stretching mode of the vinyl ester group, in agreement with published work.[19] If R or R' in the phosphate (II) is an aliphatic group, then $\nu_{max.}$ falls at about 1660—1670 cm.$^{-1}$. If R and R' both contain double linkages in conjugation with the central olefinic bond, then $\nu_{max.}$ is at about 1650 cm.$^{-1}$, while $\nu_{max.}$ is 1630—1640 cm.$^{-1}$ if R contains conjugated unsaturation and R' = H.

EXPERIMENTAL

Infrared spectra were determined on a Beckman IR5 recording spectrophotometer in potassium bromide (solids) or as films (liquids). Microanalyses were by the Microanalytical Laboratory, Department of Chemistry, University of California, Berkeley 4.

Diethyl trans-2-*Ethoxycarbonyl*-1-*phenylvinyl Phosphate* (IIa).—The sodium enolate of ethyl

[14] Jacobs and Dankner, *J. Org. Chem.*, 1957, **22**, 1424.
[15] Fleming and Harley-Mason, *Proc. Chem. Soc.*, 1961, 245; *Chem. and Ind.*, 1962, 560.
[16] Trippett, *J.*, 1962, 2337.
[17] Imai, *J. Pharm. Soc. Japan*, 1956, **76**, 405.
[18] Fleming and Harley-Mason, *Chem. and Ind.*, 1962, 561.
[19] Hall, Philpotts, Stern, and Thain, *J.*, 1951, 3341; Dege, Harris, and Mackenzie, *J. Amer. Chem. Soc.*, 1959, **81**, 3374; Meakins, *J.*, 1953, 4170; Davison and Bates, *J.*, 1953, 2607; Butler, *J. Amer. Chem. Soc.*, 1955, **77**, 482.

benzoylacetate was prepared by distilling approximately half the solvent from a stirred suspension of sodium ethoxide (3·4 g., 0·05 mole) and ethyl benzoylacetate (9·6 g., 0·05 mole) in dry benzene (500 ml.). Diethyl phosphorochloridate (8·7 g., 0·05 mole) was added and the mixture stirred under reflux for 2 hr. The cooled (0°) benzene solution was washed with 5% aqueous sodium hydroxide (100 ml.) and water, dried (Na_2SO_4), and evaporated *in vacuo*. Distillation afforded *diethyl trans-2-ethoxycarbonyl-1-phenylvinyl phosphate* (12·3 g., 75%), b. p. 151—153°/0·005 mm., n_D^{25} 1·5135 (Found: C, 54·6; H, 6·2. $C_{15}H_{21}O_6P$ requires C, 54·85; H, 6·45%), $\nu_{max.}$ 1648 cm.$^{-1}$ (C=C·O).

Diethyl cis-2-Ethoxycarbonyl-1-phenylvinyl Phosphate (IIa).—Triethyl phosphite (9·9 g., 0·06 mole) and ethyl α-chlorobenzoylacetate (11·35 g., 0·05 mole) were heated on the steam-bath for 2 hr. Distillation afforded *diethyl cis-2-ethoxycarbonyl-1-phenylvinyl phosphate* (14·5 g., 88%), b. p. 147—149°/0·005 mm., n_D^{25} 1·5075, $\nu_{max.}$ 1650 cm.$^{-1}$ (Found: C, 54·6; H, 6·45. $C_{15}H_{21}O_6P$ requires C, 54·85; H, 6·45%) (lit.,[20] b. p. 151—153°/0·35 mm., $n_D^{22.5}$ 1·5140).

Diphenyl trans-2-Ethoxycarbonyl-1-phenylvinyl Phosphate.—Reaction of the sodium enolate of ethyl benzoylacetate with diphenyl phosphorochloridate (13·5 g., 0·05 mole) afforded *diphenyl trans-2-ethoxycarbonyl-1-phenylvinyl phosphate* (16·8 g., 80%) as needles (from ethanol), m. p. 57—58° (Found: C, 65·15; H, 5·05. $C_{23}H_{21}O_6P$ requires C, 65·1; H, 5·0%), $\nu_{max.}$ 1650 cm.$^{-1}$.

Diethyl trans-1,2-Di-p-methoxyphenylvinyl Phosphate (IIb).—Approximately half the solvent was distilled from a stirred suspension of sodium ethoxide (3·4 g., 0·05 mole) and deoxyanisoin (12·8 g., 0·05 mole) in benzene (500 ml.). Diethyl phosphorochloridate (8·7 g., 0·05 mole) was added and the mixture stirred under reflux for 2 hr. The cooled mixture was washed with 5% sodium hydroxide solution (100 ml.) and water, dried (Na_2SO_4), and evaporated *in vacuo*. The residue was taken up in ethanol (60 ml.) and kept overnight at 5°. The crystals obtained were recrystallised from ethanol, affording deoxyanisoin (4·6 g.) m. p. and mixed m. p. 108—110°. The mother-liquors from the first crystallisation were evaporated *in vacuo* and the residue crystallised from hexane, affording *diethyl trans-1,2-di-p-methoxyphenylvinyl phosphate* (9·8 g.) as needles, m. p. 86—87° (Found: C, 60·9; H, 6·5. $C_{20}H_{25}O_6P$ requires C, 61·2; H, 6·45%), $\nu_{max.}$ 1615 cm.$^{-1}$.

Diethyl cis-1,2-Diphenylvinyl Phosphate (IIc).—Reaction of triethyl phosphite (9·9 g., 0·06 mole) with α-chlorodeoxybenzoin [21] (11·5 g., 0·05 mole) afforded *diethyl cis-1,2-diphenylvinyl phosphate* (13·1 g., 85%), b. p. 161—163°/0·005 mm., n_D^{25} 1·5625 (Found: C, 64·8; H, 6·3. $C_{18}H_{21}O_4P$ requires C, 65·05; H, 6·4%), $\nu_{max.}$ 1650 cm.$^{-1}$.

1,3-Diphenyl-1-chloroacetone.—Sulphuryl chloride (14·9 g., 0·11 mole) in carbon tetrachloride (50 ml.) was added during 1 hr. to a stirred solution of dibenzyl ketone (21·0 g., 0·10 mole) in carbon tetrachloride (100 ml.), and the mixture stirred for a further 3 hr., the temperature being maintained at 25—30° during the entire reaction. The solution was washed with saturated aqueous sodium hydrogen carbonate, then with water, and dried (Na_2SO_4), and the solvent was removed *in vacuo*. Crystallisation of the residue from hexane afforded *1,3-diphenyl-1-chloroacetone* (18·6 g., 76%) as needles, m. p. 65—66° (Found: C, 73·7; H, 5·5. $C_{15}H_{13}ClO$ requires C, 73·6; H, 5·35%).

Diethyl cis-α-Benzylstyryl Phosphate (IIf).—Reaction of triethyl phosphite (9·9 g., 0·06 mole) with 1,3-diphenyl-1-chloroacetone (12·3 g., 0·05 mole) afforded the *phosphate* (15·1 g., 87%), b. p. 165—167°/0·005 mm., n_D^{25} 1·5415 (Found: C, 65·9; H, 6·5. $C_{19}H_{23}O_4P$ requires C, 65·9; H, 6·7%), $\nu_{max.}$ 1666 cm.$^{-1}$.

Diethyl 1-Phenylvinyl Phosphate (IId).—Reaction of triethyl phosphite (9·9 g., 0·06 mole) with phenacyl chloride (7·7 g., 0·05 mole) afforded the phosphate (10·9 g., 85%), b. p. 101—103°/0·005 mm., n_D^{25} 1·5010 (lit.,[6] b. p. 106—107°/0·1 mm., n_D^{20} 1·5026), $\nu_{max.}$ 1640 cm.$^{-1}$.

Diethyl 1-(4-Biphenylyl)vinyl Phosphate (IIe).—Reaction of triethyl phosphite (9·9 g., 0·06 mole) with 4-phenylphenacyl chloride (11·6 g., 0·05 mole) afforded the *phosphate* (15·0 g., 90%), b. p. 184—186°/0·005 mm., n_D^{25} 1·5680 (Found: C, 64·75; H, 6·5. $C_{18}H_{21}O_4P$ requires C, 65·05; H, 6·4%), $\nu_{max.}$ 1640 cm.$^{-1}$.

Diethyl cis-α-Methylstyryl Phosphate (IIg).—Reaction of triethyl phosphite (9·9 g., 0·06 mole) with 1-chloro-1-phenylacetone [22] (8·5 g., 0·05 mole) afforded the *phosphate* (11·7 g., 86%), b. p. 108—110°/0·005 mm., n_D^{25} 1·5060 (Found: C, 57·45; H, 6·85. $C_{13}H_{19}O_4P$ requires C, 57·75; H, 7·1%), $\nu_{max.}$ 1670 cm.$^{-1}$.

[20] Nishizawa, *Bull. Agric. Chem. Soc. Japan*, 1960, **24**, 261.
[21] Ward, *Org. Synth.*, 1932, **12**, 20.
[22] Kopf, *Bull. Soc. chim. France*, 1954, 628.

Diethyl 1-*Benzylvinyl Phosphate* (IIh).—Reaction of triethyl phosphite (9·9 g., 0·06 mole) with benzyl chloromethyl ketone [23] (8·5 g., 0·05 mole) afforded *diethyl* 1-*benzylvinyl phosphate* (11·8 g., 87%), b. p. 109—110°/0·005 mm., n_D^{25} 1·4840 (Found: C, 57·75; H, 6·9. $C_{13}H_{19}O_4P$ requires C, 57·75; H, 7·1%), $\nu_{max.}$ 1660 cm.$^{-1}$.

Diethyl cis-1-*Phenylpropenyl Phosphate* (IIi).—Reaction of triethyl phosphite (9·9 g., 0·06 mole) with 1-phenyl-2-chloropropan-1-one [24] (8·5 g., 0·05 mole) afforded *diethyl* cis-1-*phenyl-propenyl phosphate* (11·5 g., 85%), b. p. 114—116°/0·005 mm., n_D^{25} 1·5030 (Found: C, 57·45; H, 7·15. $C_{13}H_{19}O_4P$ requires C, 57·75; H, 7·1%), $\nu_{max.}$ 1670 cm.$^{-1}$.

General Method of Preparation of Acetylenes and Allenes from Enol Phosphates.—A solution of the enol phosphate (0·02 mole) in ether (50 ml.) was added during 10 min. to a stirred suspension of sodamide (from 2·3 g. of sodium) in liquid ammonia (200 ml.). After 2 hours' stirring under reflux ammonium chloride was added and the ammonia allowed to evaporate. The residue was distributed between ether and water, and the ether layer was separated, dried (Na$_2$SO$_4$), and evaporated. The product was purified by crystallisation, by preparation of the mercury salt, or by distillation. The results are summarised in the Table.

Formation of acetylenes (III) and allenes (IV) from enol phosphates (II) at −33°.

Enol phosphate	Product	M. p. (etc.)	Yield (%)	Recorded m. p. (etc.)
trans-(IIa)	(IIId) *	123—124°	75	[25] 123—124°
trans-(IIa) †	(IIIk)	—	72	—
cis-(IIa)	(IIId) *	123—124	65	[25] 123—124
cis-(IIa) †	(IIIk)	—	12	—
	cis-(IIa)	—	80	—
Ph$_2$ *trans*-2-ethoxycarbonyl-1-phenylvinyl phosphate	(IIId) *	123—124	70	[25] 123—124
trans-(IIb)	(IIIb)	142—143	94	[26] 142—143
cis-(IIc)	(IIIc)	60—61	90	[27] 60—61
(IId)	(IIId) *	123—124	75	[25] 123—124
(IIe)...................................	(IIIe)	86—87	92	[14] 87
cis-(IIf) ‡	(IVc)	47—50	77	[14] 49—51
cis-(IIg)	(IVd)	(b. p. 80—82°/25 mm., n_D^{25} 1·5770)	75	[28] (b. p. 72°/17 mm., n_D^{20} 1·5820)
(IIh)	(IVd)	(b. p. 84—86°/30 mm., n_D^{25} 1·5775)	77	—
cis-(IIi)		No allene or acetylene obtained		

* Isolated as mercury derivative. † Experiment at −70°. ‡ Reaction time 10 min.

Phenylpropiolamide.—A suspension of sodamide (from 2·3 g. of sodium) was prepared in a 1-l. 3-necked flask fitted with a stirrer, a condenser cooled with solid carbon dioxide, and a dropping funnel whose stem reached well into the flask. The flask was immersed in a deep bath which was kept at −78° during the entire reaction.

Diethyl *trans*-2-ethoxycarbonyl-1-phenylvinyl phosphate (6·56 g., 0·02 mole) in ether (50 ml.) was added during 30 min., and after a further 1·5 hr. ammonium chloride was added. The ammonia was allowed to evaporate, water was added, and the product isolated with ether. Crystallisation from benzene afforded phenylpropiolamide (2·05 g., 72%), m. p. and mixed m. p. 107—108°.

1-*Chloropent*-3-*yn*-2-*one.*—A suspension of sodiopropyne (from 13 g. of sodium) in ether (150 ml.) was added during 1 hr. to a stirred solution of chloroacetyl chloride (28·3 g., 0·25 mole) in ether (100 ml.). The mixture was stirred under reflux for a further 3 hr., cooled, and cautiously decomposed with dilute sulphuric acid. The ether layer was separated, washed with water, then with saturated sodium hydrogen carbonate solution, dried (Na$_2$SO$_4$), and evaporated. Distillation afforded 1-*chloropent*-3-*yn*-2-*one* (18·6 g., 63%), b. p. 84—86°/25 mm., n_D^{25} 1·4840 (Found: C, 51·05; H, 4·5. C_5H_5ClO requires C, 51·05; H, 4·3%), $\nu_{max.}$ 2222 (C≡C), 1690 and 1680 cm.$^{-1}$ (split C=O).

Diethyl 1-*Prop*-1′-*ynylvinyl Phosphate* (IIj).—A solution of triethyl phosphite (24·9 g., 0·15

[23] McPhee and Klinsberg, *Org. Synth.*, 1946, **26**, 13.
[24] Baker and Barkenbus, *J. Amer. Chem. Soc.*, 1936, **58**, 263.
[25] Johnson and McEwen, *J. Amer. Chem. Soc.*, 1926, **48**, 469.
[26] Wiechell, *Annalen*, 1894, **279**, 338.
[27] Fittig, *Annalen*, 1873, **168**, 74.
[28] Gaudemar, *Ann. Chim. (France)*, 1956 [13], **1**, 161.

mole) in benzene (50 ml.) was heated to reflux temperature, the source of heat removed, and 1-chloropent-3-yn-2-one (17·6 g., 0·15 mole) added at such a rate as to cause gentle reflux (∼15 min.). The mixture was refluxed for a further 30 min. Distillation afforded *diethyl 1-prop-1'-ynylvinyl phosphate* (22·3 g., 68%), b. p. 96—98°/0·005 mm., n_D^{25} 1·4540 (Found: C, 49·25; H, 6·8. $C_9H_{15}O_4P$ requires C, 49·55; H, 6·9%), $\nu_{max.}$ 2240 (C≡C) and 1630 cm.$^{-1}$ (C=C·O).

1-*Phenylhexa*-2,4-*diyn*-1-*ol*.—A solution of diethyl 1-prop-1'-ynylvinyl phosphate (21·8 g., 0·10 mole) in ether (50 ml.) was added during 15 min. to a stirred suspension of sodamide (from 5·8 g. of sodium) in liquid ammonia (350 ml.). A solution of benzaldehyde (10·8 g., 0·10 mole) in ether (50 ml.) was then added during 15 min. and the mixture stirred under reflux for a further 8 hr. Ammonium chloride was added, the ammonia allowed to evaporate, and the residue distributed between ether and water. Distillation of the dried (Na_2SO_4) ether layer afforded an oil, b. p. 145—150° (bath)/0·005 mm., which on crystallisation from hexane afforded 1-phenylhexa-2,4-diyn-1-ol (7·0 g., 41%) as needles, m. p. 83—84° (not raised by recrystallis-ation) (lit.,[17] 87°) (Found: C, 84·4; H, 6·0. Calc. for $C_{13}H_{10}O$: C, 84·7; H, 5·9%), $\nu_{max.}$ 2260, 2222 cm.$^{-1}$ (C≡C).

DEPARTMENT OF PHARMACEUTICAL CHEMISTRY, UNIVERSITY OF CALIFORNIA,
SAN FRANCISCO 22, U.S.A.