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OLD AND NEW YLID CHEMISTRY

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Abstract - A. The mechanism of the Wittig reaction is re-interpreted on the
basis of new experimental and theoretical results.
B. Reactions of trimethylsilylated phosphorus ylides are described. They
allow a reversal of the stereochemistry of the Wittig reaction.
C. The preparative possibilities of the reaction of N-phenyl-ketenylidene-
triphenylphosphorane with carbon acids are presented and the synthesis of the
tetramer of phenyl isonitrile is reported.
D. The results of investigations into the reactions of Hexaphenylcarbodi-
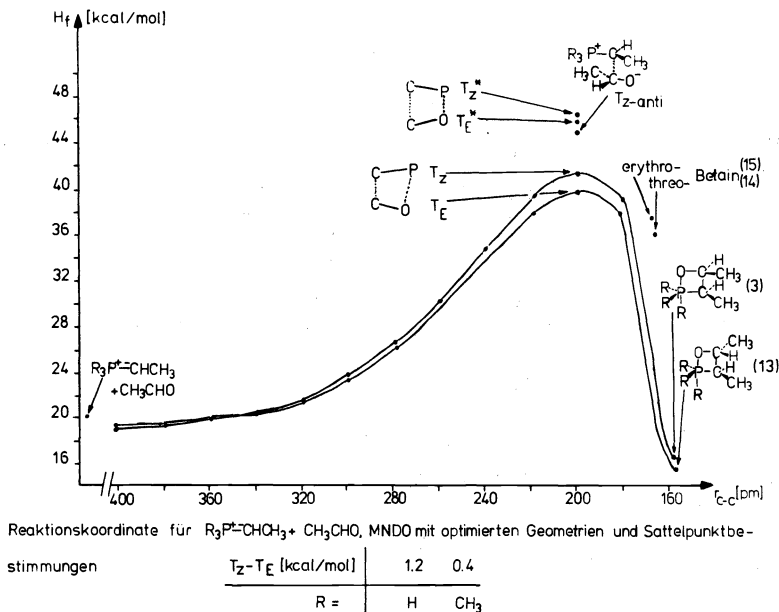phosphorane are presented.

A. The Wittig Reaction

Detailed investigations have led us to propose a new mechanism for the Wittig
reaction.[1)2)3)] Ylides, (1), and aldehydes, (2), combine to give oxa-
phosphetanes, (3), in which the O-atom occupies an apical position on the
pentavalent phosphorus and in which the substituents on the four membered
ring are Z to one another. Cleavage of the original ylid C-P bond, which is
necessary for formation of the olefin, requires a ligand reorganisation
process (pseudorotation) which brings this bond to an apical position.[4)]

The opening of the C-P bond to give the betain (5) occurs during or after the
conversion to the trigonal bipyramidal structure (4). The electronic nature
of the substituents R^1 and R^2 in (5) is instrumental in determining the
stereochemistry of the product olefin. When R^1 = phenyl electron donating
R^2 substituents cause a very fast elimination of the phosphine oxide, giving
Z olefins (7). Electron-withdrawing R^2 groups (R^1=phenyl) extend the life-
time of (5), which can now isomerise to the thermodynamically more stable
(6), from which phosphine oxide elimination gives E-olefins (8). If the
ligands R^1 on phosphorus are electron-donating the rate of the phosphine
oxide elimination is also decreased. In this case strongly increased
formation of E-olefins is observed, compared to R^1=C_6H_5, even when R^2 is an
electron donor.
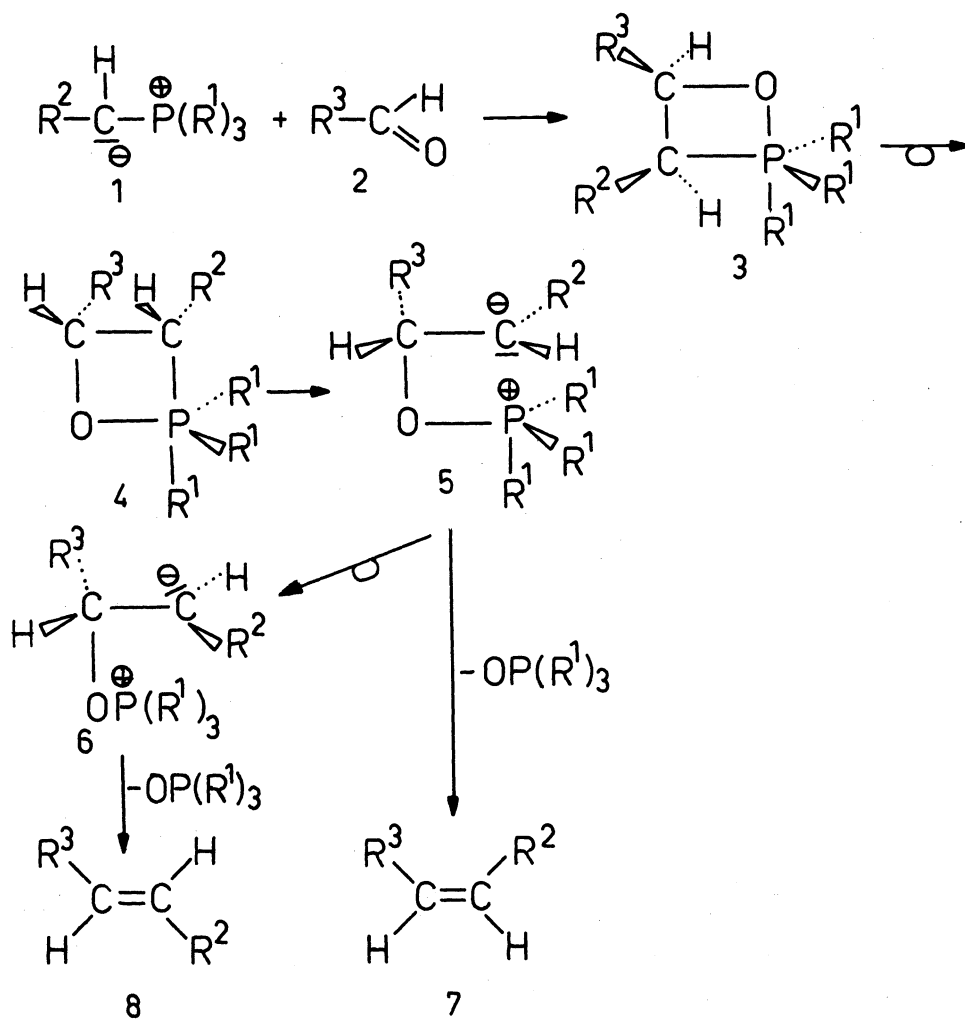
The mechanism and the stereochemical grounds for the formation of (3) with R^2 and R^3 Z to each other remain unexplained. We have therefore calculated the reaction path,[6] to test the hypothesis that at a C-C distance of 300 pm between ylid and carbonyl compound the approach angle is $107°$ [5] using MNDO semi-empirical molecular orbital theory.[7]

Reaktionskoordinate für $R_3P^+\text{=CHCH}_3 + CH_3CHO$, MNDO mit optimierten Geometrien und Sattelpunktbestimmungen

T_Z-T_E [kcal/mol]	1.2	0.4
R =	H	CH₃

- FIGURE 1-

Figure I shows the results of these calculations for $H_3\overset{\oplus}{P}\text{-}\overset{\ominus}{C}H\text{-}CH_3$ as the ylid and aceteldehyde as the carbonyl compound. Four different starting conformations were used at a C-C distance of 400 pm as starting points for the approach of the two reactants.
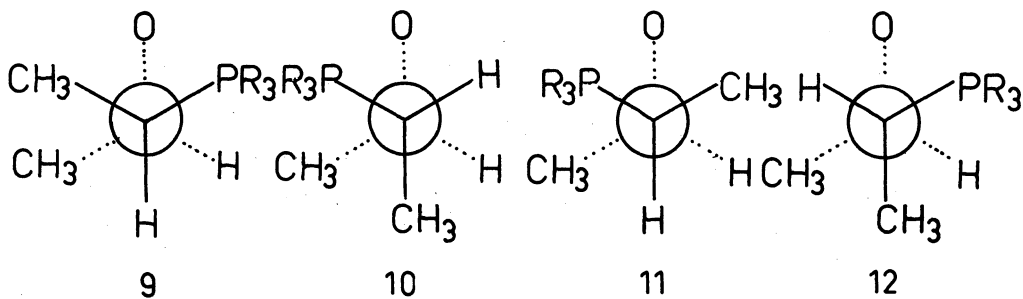
(9) and (10) lead to oxaphosphetanes with the methyl groups Z to one another, (11) and (12) give the E-isomers.

The C-C distance was decreased progressively by 20 pm and all other parameters optimised. This procedure showed that conformation (10) collapsed to (9) and (12) to (11). Although (9) is slightly lower in energy than (11) at a C-C distance of 400 pm the reverse is true by 1.2 kcal mol^{-1} (5 kJ mol^{-1}) at the transition state near 200 pm. The E-oxaphosphetane is calculated to be 1.3 kcal mol^{-1} (5.4 kJ mol^{-1}) more stable than the Z-isomer.

When the hydrogen atoms on phosphorus are replaced in the calculations by methyl groups the energy difference between the two transition states T_E-T_Z sinks to 0.4 kcal mol^{-1} (1.7 kJ mol^{-1}). These results disagree, to a certain extent, with the experimentally found preference for Z-stereoselectivity

discussed above, which suggests that the Z-transition state (T_Z) is 1.5 kcal mol^{-1} more stable than the E-transition state (T_E).

The errors inherent in the calculational method[7] can, however, account for this discrepancy. Our calculations show, however, that the geometry of approach used here gives energy differences of the correct order of magnitude.

Figure 1 also shows the energies of the erythro- and threo-betains (15) and (14) for comparison with the Z- and E-oxaphosphetanes (3) and (13).
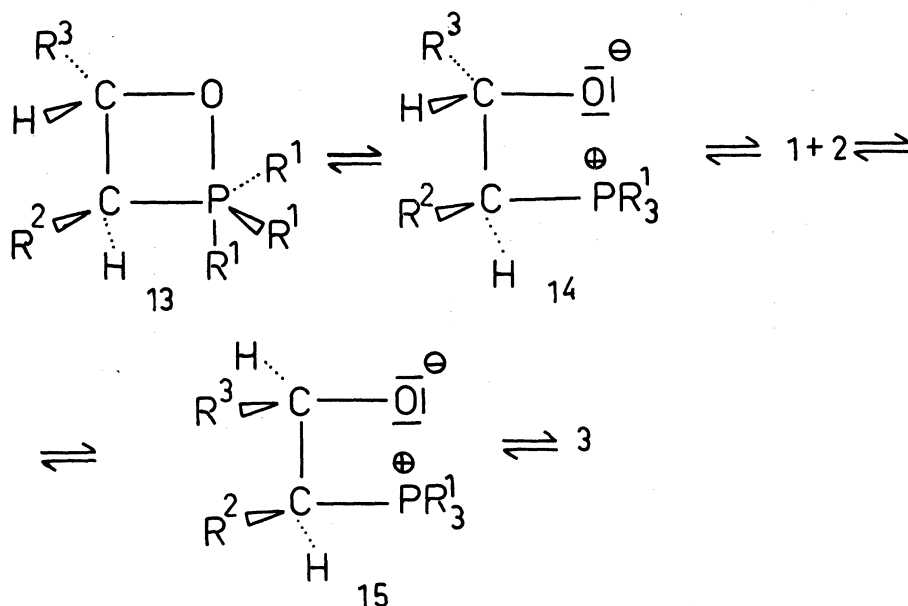

The open-chain adducts (15) and (14) were once considered[8] to be real inter-mediates in the Wittig reaction and an equilibrium between (15) and (14) via ylid, (1), and carbonyl compound, (2), was used to explain the loss of Z-stereoselectivity with more stable phosphoranes (R^2=aryl, COOR, CN, etc.). The fully optimised betains, (15), are calculated to be 20 kcal mol^{-1} (84 kJ mol^{-1}) less stable than the corresponding oxaphosphetanes, (3) and (13), however. This large calculated energy difference between the four membered rings, which are the only spectroscopically observable intermediates in the Wittig reaction,[2,8d,9] and the betains, and between the oxa-phosphetanes and their components, (1) and (2), exclude reversible equilibria, and mechanisms based on such equilibria. This is in agreement with the fact that the oxaphosphetanes, (3), (R^2=alkyl, R^1=phenyl) have been shown by ^{31}P nmr[2)9)] to be stable at low temperatures, whereas those derived from stable ylids (R^2=electron accepting) have not been observed.

Contrary to these results, the previously discussed mechanisms have postulated a very fast decomposition of the intermediate to form Z-olefins in order to

explain kinetically controlled Z-stereoselectivity. The lifetime of the
betaines for stable phosphoranes is then proposed to be long enough to allow
thermodynamic equilibriation.

An equilibrium between oxaphosphetanes (16) and (18) via a betain (17) has
been ruled out by Corey[10] as the product alcohols, (19) and (20), show
deuterium labelling only in the positions shown in the Scheme. If the betain
(17) were present in the equilibrium, mixtures of alkenes (19) and (20) would
be expected for both Wittig reactions.
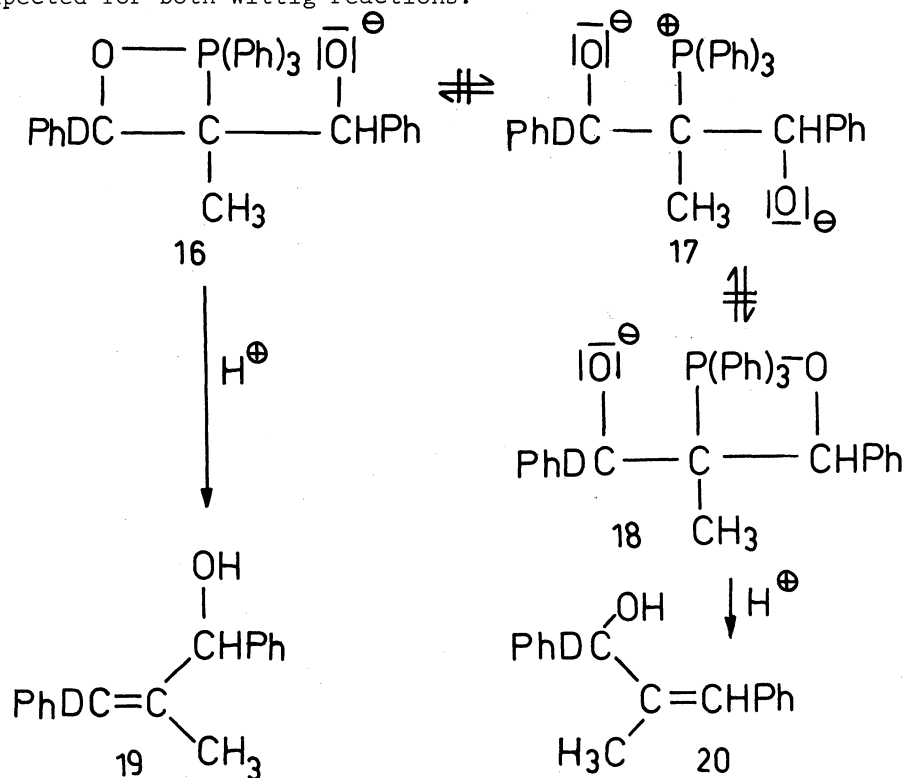
A recently published[11] analogous experiment with formaldehyde gave, in
contrast, a mixture of olefins as product. However, as the allyl alcohols
were worked-up in the presence of potassium t-butylate, deuterium exchange
between the acidic allyl positions cannot be excluded.

We have also calculated the transition states, T_Z^* and T_E^* (shown in Figure
1), for initial formation of the P-O bond, which have also been discussed in
the literature[12]. Diagonalisation of the fone-constant matrix shows that
only T_Z and T_E, which are 6 kcal mol^{-1} more stable than T_Z^* and T_E^* are true
transition states. This is not the case for T_Z^* and T_E^*.

A betain in which the two polar groups are anti (T_Z-anti in Figure 1), which
has also been discussed[13], is also calculated to be higher in energy than
T_Z and T_E. The fact that high Z-stereoselectivity for R^2=alkyl is observed
in both non-polar solvents[8a)14)] and in the highly polar hexamethyl-
phosphortriamide[15] (i.e. the stereoselectivity of the reaction is largely
independent of solvent polarity) also speaks against such a transition state.
Figure 2 shows the calculated geometry of the transition state T_Z.
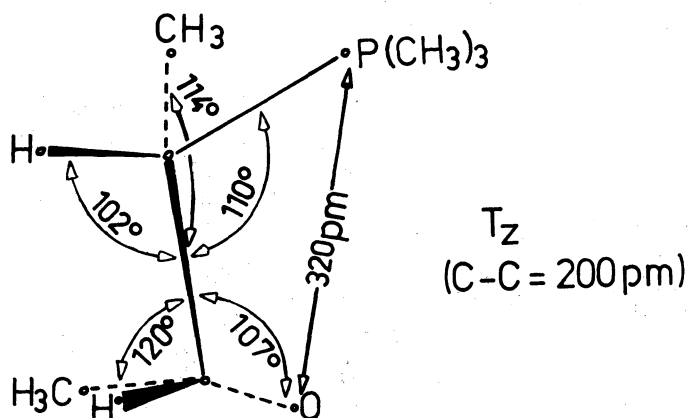
- Figure 2 -

It is clear that the idea that the nucleophile (ylid, 1) does not approach
the carbonyl group at an angle of $90°$, as developed by Bürgi, Dunitz, Lehn
and Wipf,[5] is applicable to reactions 1 and 2. The C-C bond in T_Z is more
nearly formed than the P-O (P-O distance = 320 pm). This means that the
reaction proceeds via a quasi-betain transition state, which, however, does
not lead to an intermediate betain but to an oxaphosphetane. Transition
state theory rules out an equilibrium between reactants and the activated
complex. A more sterically demanding transition state, which leads to (3)
via a (π2a + π2s)-cycloaddition of (1) and (2)[9] appears unlikely.

As our proposed mechanism for the Wittig reaction requires a ligand re-
organisation process from (3) to (4) we have used ab initio molecular orbital
theory to calculate the energy difference between (3) and (4) ($R^1=R^2=R^3=H$).
(3) is calculated to be 7.6 kcal mol^{-1} (31.9 kJ mol^{-1}) more stable than (4)
using the split-valence 4-31G[16] basis set. This value is considerably
smaller than previously assumed.[17]

The X-ray structure of a primary adduct, (23), from the cyclic phosphacumulene
ylid, (21),[18] and fluorenone (22) is now available,[19] and confirms the
bipyramidal geometry of type (3) with apical oxygen.
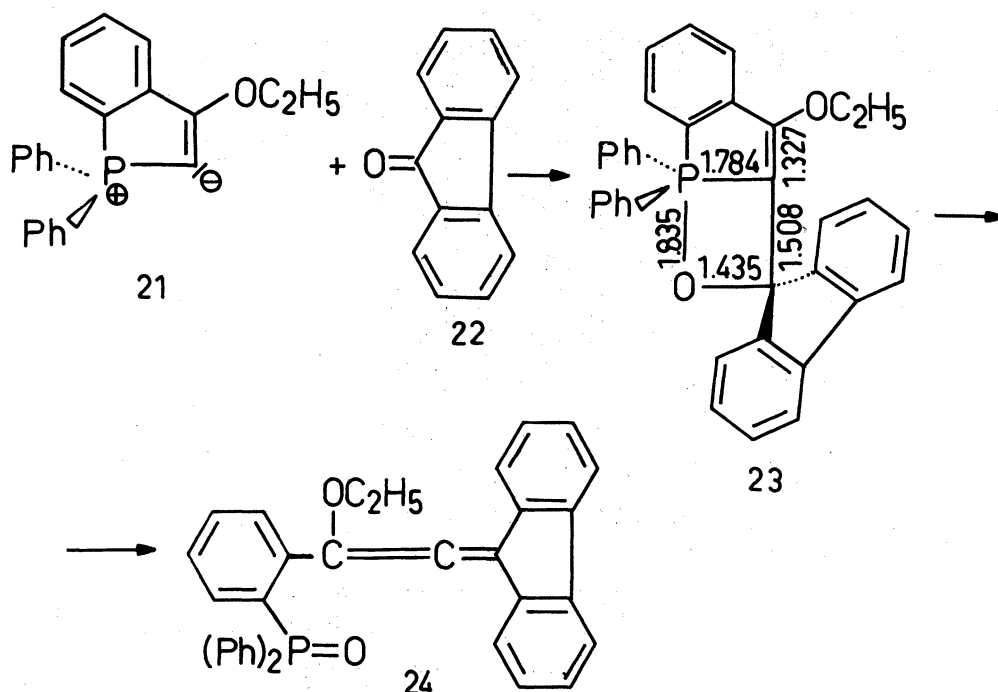
(23) decomposes only after several hours in boiling toluene or oupon heating above the melting point. The products are partly the starting compounds, (21) and (22), and partly the allene, (24). We consider this to be a confirmation of the proposed ligand reorganisation process (pseudorotation) which is strongly hindered by the rigidity of the molecule in (23).

If the ylids (1) (R^2=alkyl) are reacted at -80° with carbonyl compounds to give (3) with subsequent addition of several equivalents of ethanol, the Z-stereoselectivity is lost. An increase in E-olefins to over 50% is observed.[2] If deuterium or tritium labelled alcohol is used the label is incorporated to a large extent in the product olefin, but considerably more in the E- than in the Z-isomers. Based on these new investigations we propose the following reaction mechanism:
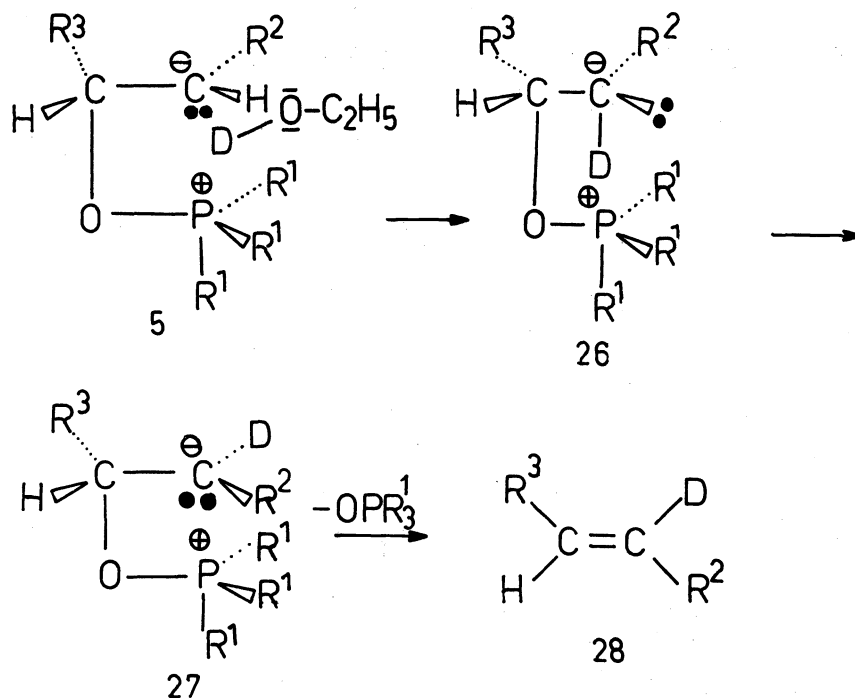
The betain (5), which may exist as a contact ion pair and represents on inter-
mediate in the E_{1cB} elimination, reacts with the alcohol to give (26) via
synchronous addition and elimination of a deuterium and a proton.[20] The
betain (26) is formed and then largely converts to conformation (27), which
is energetically more favourable for the contact ion pair. The labelled E-
olefin, (28) is formed by a syn-elimination of phosphine oxide from (27).
The preparative possibilities of this isotopic labelling in the Wittig
reaction have already been pointed out.[1b]

B. Trimethylsilylated Ylids

Trimethylsilyl ylids (30) may be prepared via the transylidation reaction[21]
from ylids (1) and trimethylsilylchloride (29).[22,23] The reaction of the
phosphoranes (30) with carbonyl compounds is reported in the literature to
be very complex and generally not to give Wittig reactions.[23a,24,25]

We have re-investigated the reaction of (30) with aldehydes and find that the
conversion of the carbonyl compound to an olefin takes place in up to 70%
yield.[26] Vinyl silanes, (31), are produced with high Z-stereoselectivity.
E-olefins, (8), can then be obtained by stereoselective desilylation with
acid.[26,27]
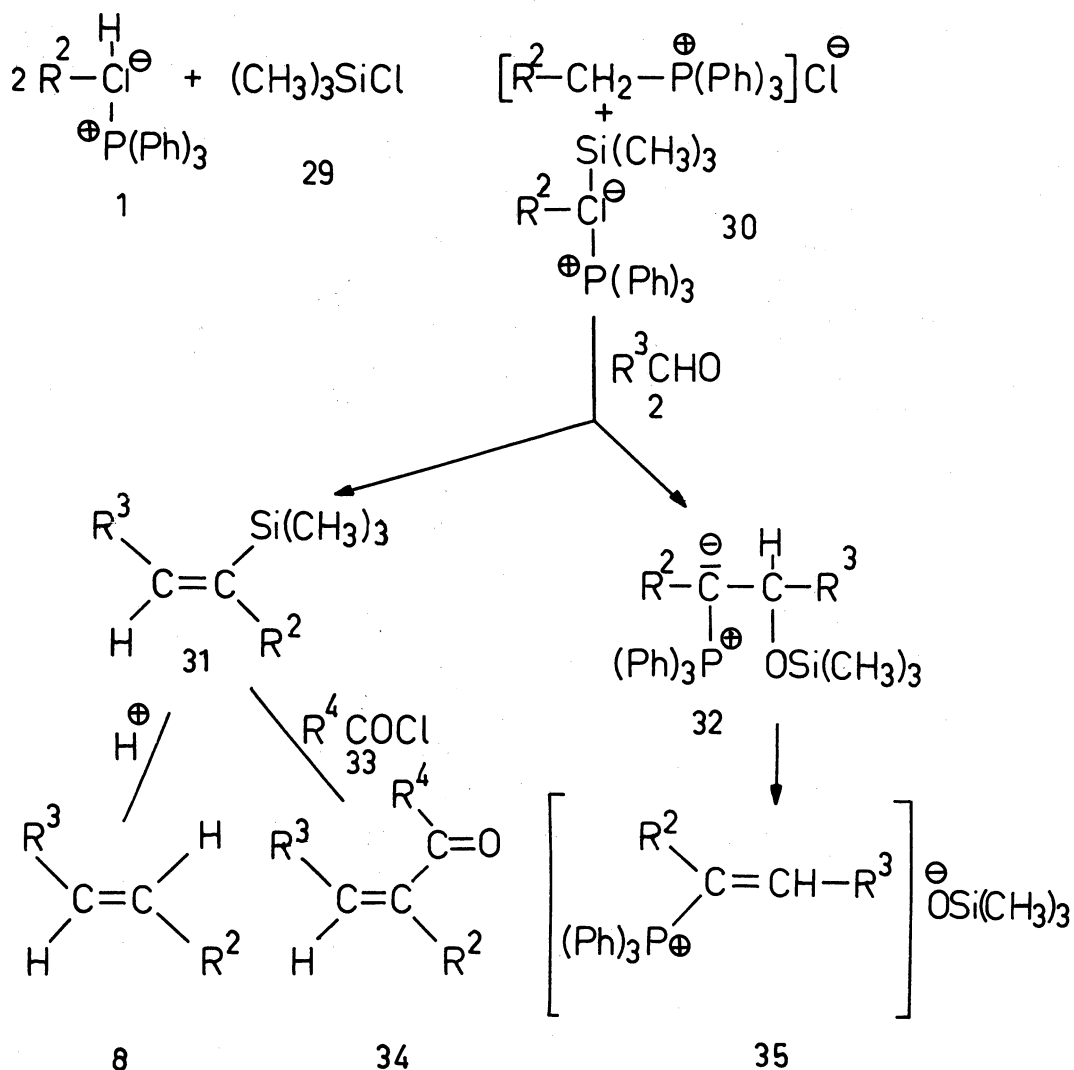
The reaction of (31) with acid chlorides, (33), in the presence of $AlCl_3$ leads to Z- ,ß-unsaturated ketones.[28]

As discussed above, the reaction of (1) (R^2=alkyl) with aldehydes, (2), yields stereo-specifically Z-olefins, whereas the reaction of aclylids (R^2=acyl) with (2) leads to E- ,ß-unsaturated ketones because of the electron-withdrawing nature of R^2. Using silylylids (30), and the resulting vinylsilanes, (31), the stereochemistry can be reversed and E-olefins, (8), and Z- ,ß-unsaturated carbonyl compounds can be produced.

We have found that when (30) and (2) are reacted up to 30% vinylphosphonium salts (35) are produced in addition to the major product (31).

These salts result from a migration of a trimethylsilyl group from carbon to oxygen.[23a)24)] The ylid thus produced, (32), then converts to the vinyl-phosphonium-trimethylsilanolate (35), in which the anion can be exchanged for halide.

The preparation of further disubstituted ylids (39) is still problematical
as the synthesis of the corresponding phosphonium salts from secondary alkyl
halides does not proceed uniformly and often yields different isomerisation
products which are formed by addition-elimination reactions.[29] Similarly
the alkylation of ylids (1) with alkyl halides does not always proceed
uniformly.[30] By use of the trimethylsilyl ylids (30) we have discovered a
simple method for the synthesis of phosphoranes (39). When the halogen
compound (37) is reacted with (30), the phosphonium salts (38) can be
isolated.[22a][31] These can be desilylated in the presence of fluoride ion.
The resulting ylids (39) can immediately be reacted _in statu nascendi_ with
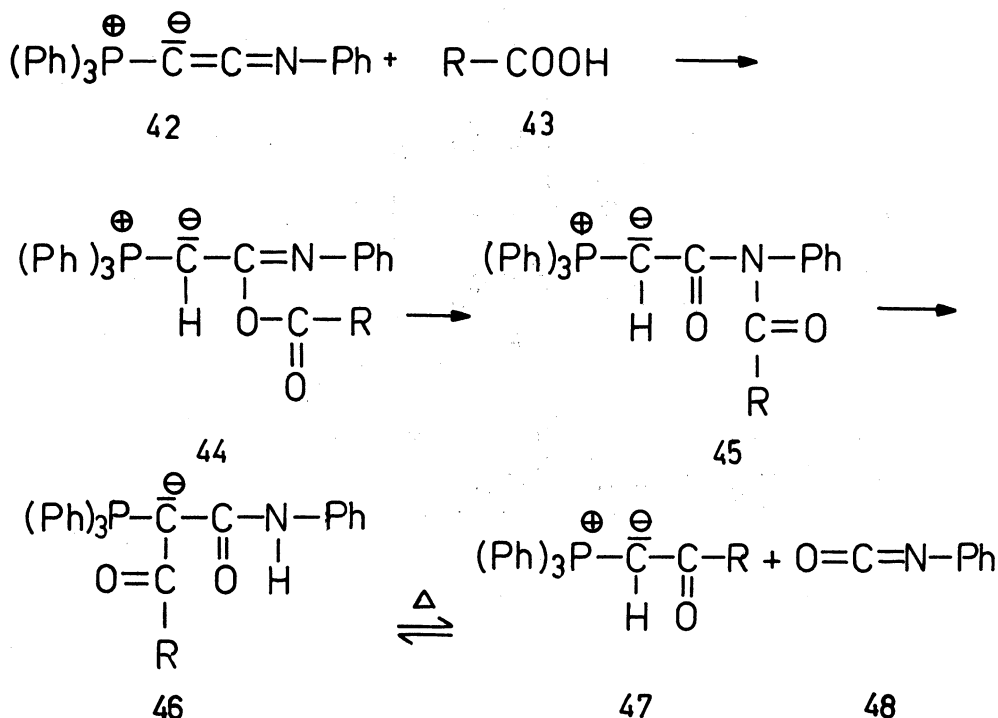aldehydes (2) to yield olefins (40).[26]
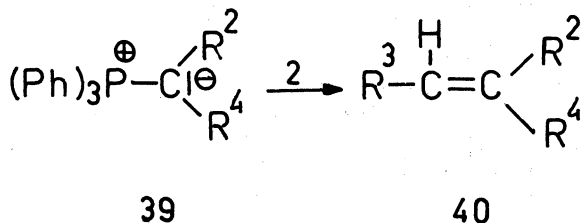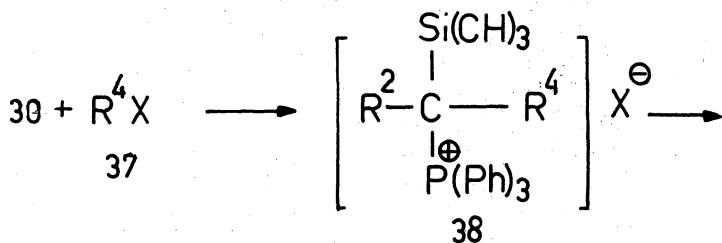
C. Phosphacumulene Ylids

We designate phosphoranes of the type (41) as phosphacumulene ylids. They can
be described by the resonance forms (41a) and (41b).

X= NR,O,S
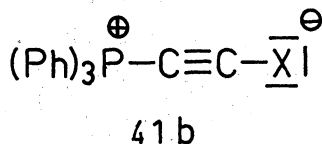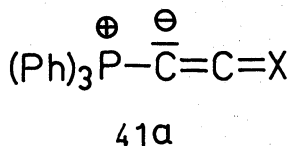
X- ray diffraction studies have shown that as the electron-withdrawing
character of X increases, and its tendency to give double bonds decreases the
reasonance form (41b) becomes more important.

The strongly nucleophilic orthoganal -system in (41) is occupied by 4
electrons (^{4} ^{4} -system). It is converted by addition of an electrophile into
the dipolar orthoganal -system of keten, with 4 electrons in one plane and 2
in the other (^{4} ^{2} -system). These properties of phosphacumulene ylids allow
a multitude of reactions which have been briefly reviewed.[32] We now present
a few new reactions.[33]

$$\overset{\oplus}{(Ph)_3P} - \overset{\ominus}{\overline{C}} = C = N - Ph \ + \ R - COOH \ \longrightarrow$$

42   43

$$\overset{\oplus}{(Ph)_3P} - \overset{\ominus}{\overline{C}} - C = N - Ph \qquad \overset{\oplus}{(Ph)_3P} - \overset{\ominus}{\overline{C}} - C - N - Ph \longrightarrow$$

44   45

$$(Ph)_3P - \overset{\ominus}{\overline{C}} - C - N - Ph \qquad \overset{\oplus}{(Ph)_3P} - \overset{\ominus}{\overline{C}} - C - R \ + \ O = C = N - Ph$$

46   47   48

Carbonic acids (43) add to N-phenyliminoketenylidene-triphenylphosphorane
(42) to give the phosphoranes (44), which rearrange to the acylamide-
phosphoranes (45) via an O-N acyl migration. With gentle warming a further
acyl group migration from the N-atom to the ylid carbon follows with a
simultaneous shift of the proton from carbon to nitrogen. The phosphorane
(46) can be isolated. This yields the acylylid (47) in an equilibrium
reaction with extrusion of phenylisocyanate (48) upon heating. (48) can
be trapped from the equilibrium with alcohols. The reaction of (42) with
(43) therefore provides a method for the conversion of carbonic acids into
acyl ylids.[34]

When (42) is reacted with -keto acids, (49), the phosphoranes (50) are
produced. In a few cases these give the substituted maleic isoimides (52)
via an intramolecular Wittig reaction. Usually (50) rearranges to (51) which
then gives the maleic imide (53) by triphenylphosphine oxide elimination. As
(52) can also be easily be converted to (53) this reaction represents a new
general method for the synthesis of compounds of the type (53).

42 + R—CO—COOH ⟶
      49

50 ⟶ **51**

50   — OP(Ph)₃ ⟶ **52** ⟶ **53**

51   — OP(Ph)₃ ⟶ **53**
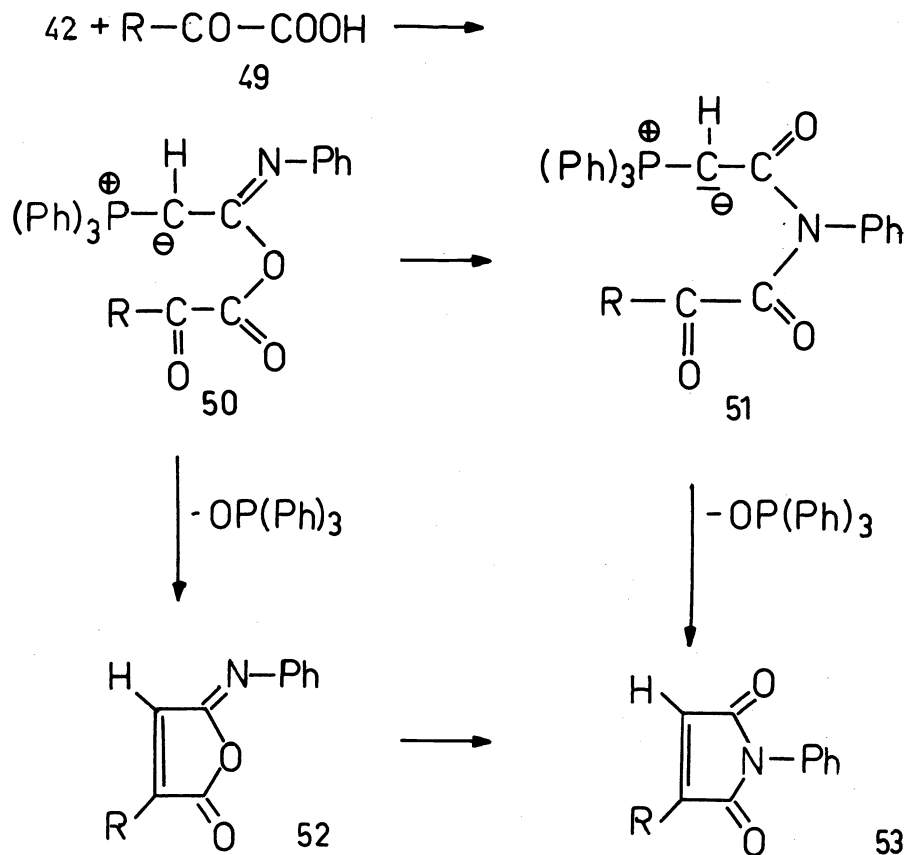
The stable ylids (55) are formed via the reaction sequence described from (42) and -keto-acids, (54). On warming they also extrude phenyl isocyanate. The resulting phosphorane (56) then enters into an intramolecular Wittig reaction to give (57). The reaction of (42) and (54) thus represents a generally applicable synthesis for substituted cyclopentenones.

42 + R—C—CH₂—CH₂—COOH ⟶
      O   54

55   — 48 ⟶ **56**

— OP(P)₃ ⟶ **57**
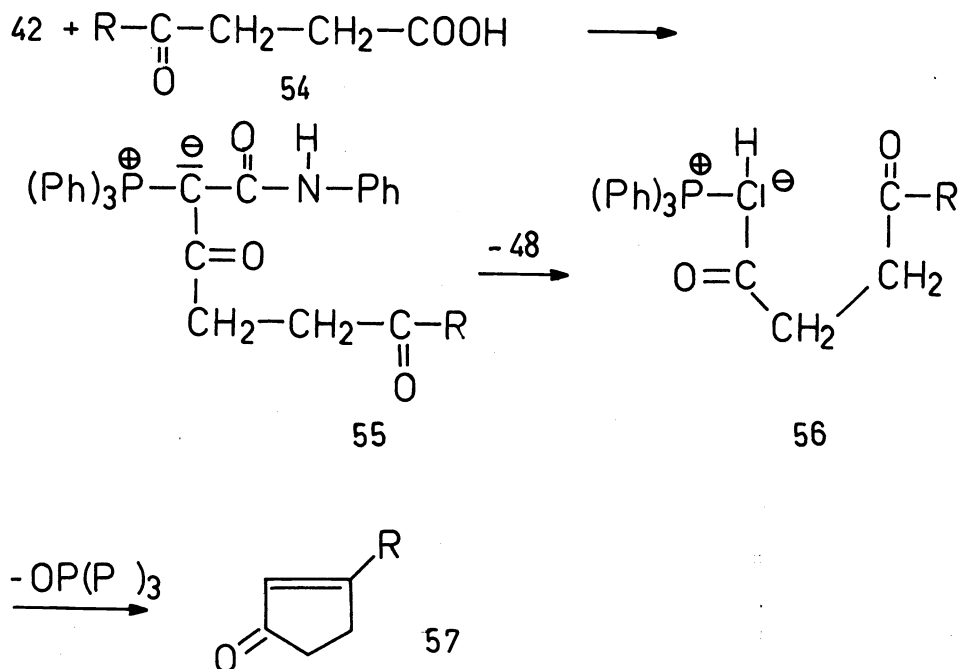
Reaction of (42) with nitroso benzene (58), leads to the formerly unknown
tetra(phenylimino)cyclobutane (63) (tetrameric phenylisonitrile)[35].

We have proposed two reaction paths but cannot yet distinguish between the
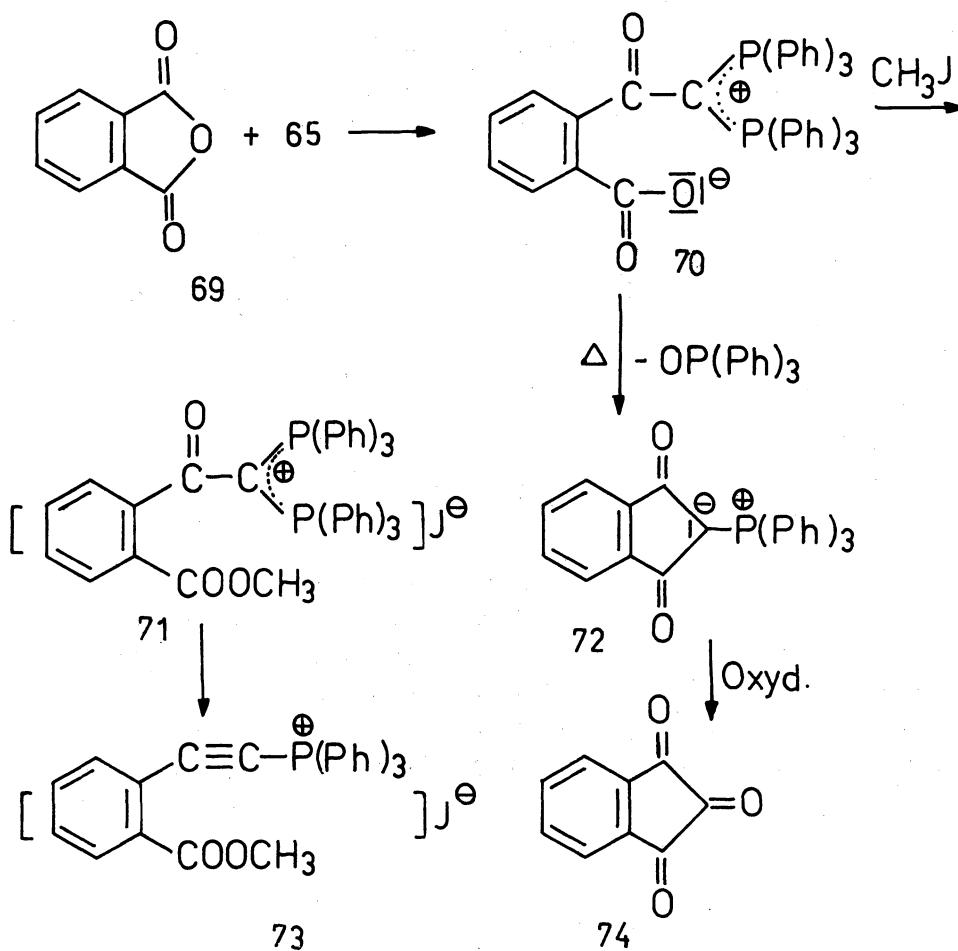two:
1. The dimeric isonitrile (61) which is formed via a Wittig reaction from
    (59), dimerises to give (63).
2. (59) gives a 2+2-cycloaddition with (42) leading to (60), which gives (62)
    by elimination of triphenylphosphine oxide. (62) then reacts with (58)
    to give (63). We also obtained (63) from reaction of the dimer of (42),
    (64[36]), with (58). An X-ray structure analysis of (63) is available[35].

$$42 + Ph-N=O \longrightarrow (Ph)_3P-C=C=N-Ph \xrightarrow{42}$$
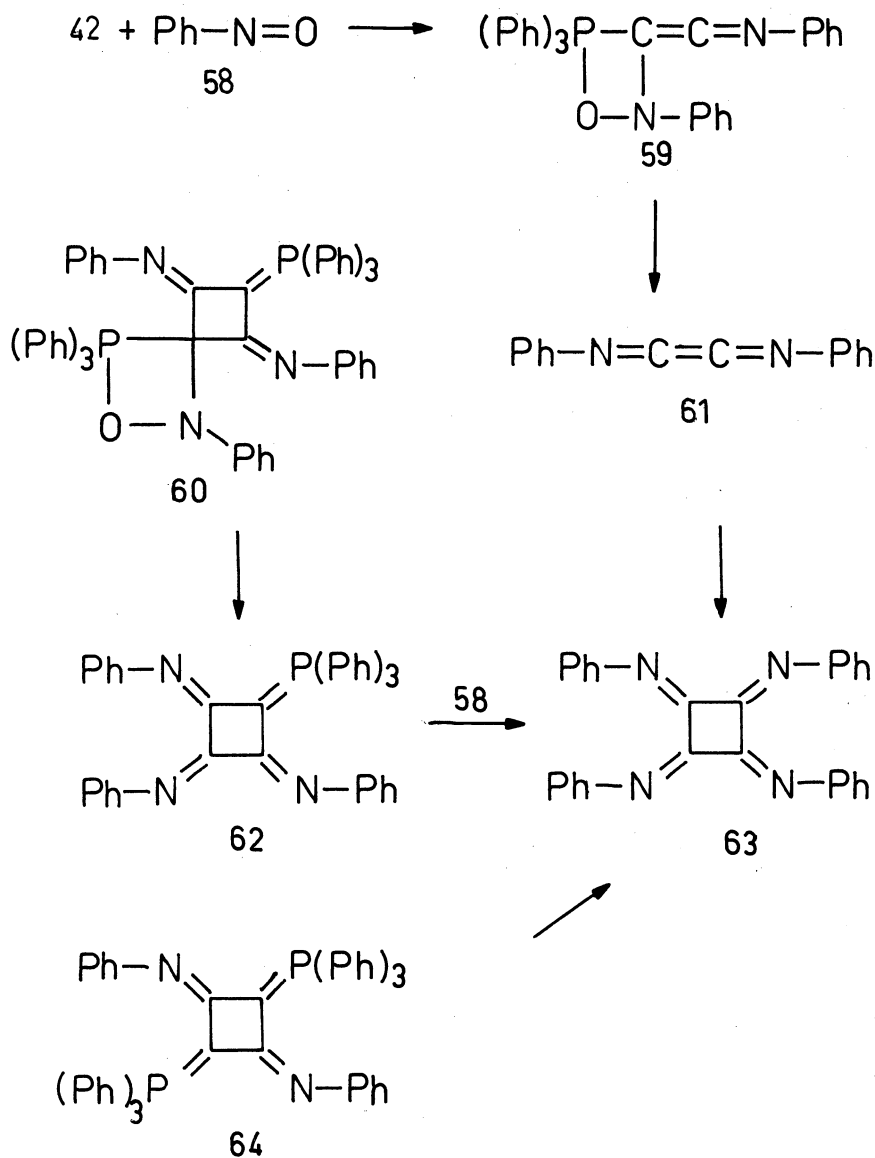
D. Hexaphenylcarbodiphosphoranes

The fascinating molecule hexaphenylcarbodiphosphorane, (65), was first
synthesized by F. Ramirez et al.,[37] and more recently by R. Appel et al.[38]
The structure and structure variations of (65) have recently been reviewed.[39]
Surprisingly the reactions of (65) have been little studied.[40]   Our
investigations in this field led to the following results:

(65) reacts with aromatic acid chlorides, (66) to give the phosphonium salts,
(67), which, upon warming, eliminate triphenylphosphine oxide to give the
preparatively interesting acetylene phosphonium salts (68).[41]

$$(Ph)_3\overset{\oplus}{P}-\overset{2\ominus}{\underset{}{C}}-\overset{\oplus}{P}(Ph)_3 \;+\; Ar-COCl \longrightarrow$$

                    65   66

$$\left[Ar-\underset{\underset{O}{\|}}{C}-C\underset{P(Ph)_3}{\overset{P(Ph)_3}{\overset{\oplus}{\diagdown}}} \right] Cl^{\ominus} \quad \xrightarrow{-OP(Ph)_3} \quad \left[Ar-C\equiv C-\overset{\oplus}{P}(Ph)_3 \right] \overset{\ominus}{Cl}$$

                    67   68

                 69   70

                                $$\Delta \Big| - OP(Ph)_3$$

           71   72

                 $$\Big| Oxyd.$$

           73   74
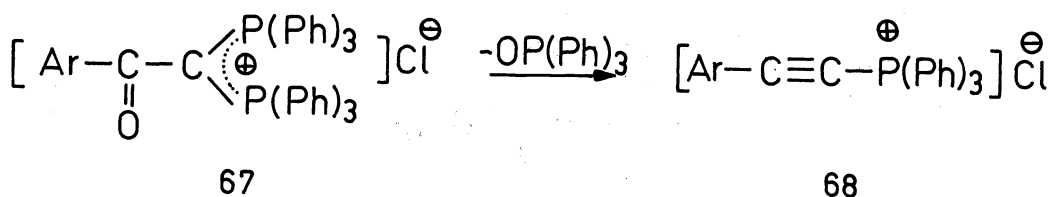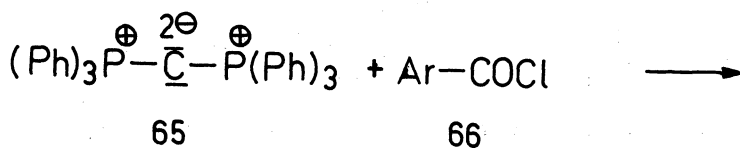
With cyclic aromatic carboxylic anhydrides, e.g.(69) and (65), a betain (70)
is first formed. This reacts with methyl iodide to give (71), which converts
extremely easily to (73). When (70) is warmed triphenylphosphine oxide
eliminates. The product is the cyclic diacyl ylid (72), which can be oxidised
to ninhydrin, (74).[42] The reaction sequence (65)→(68) represents the
exchange of an anhydride oxygen for an ylid function, and is also successful
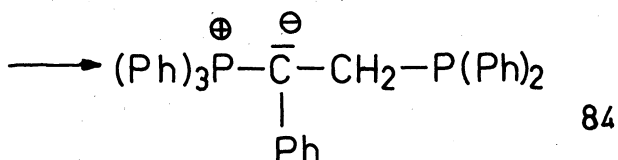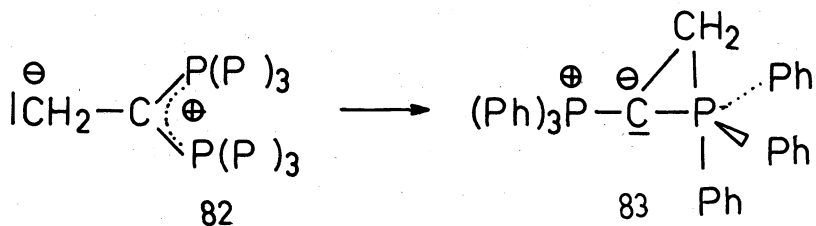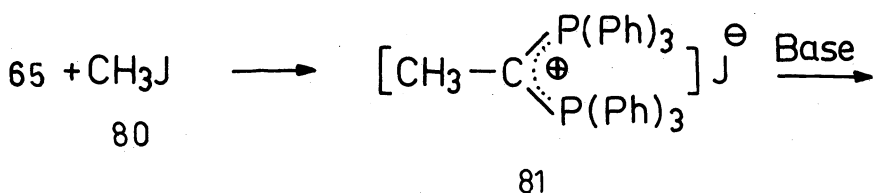for other aromatic carboxylic anhydrides.
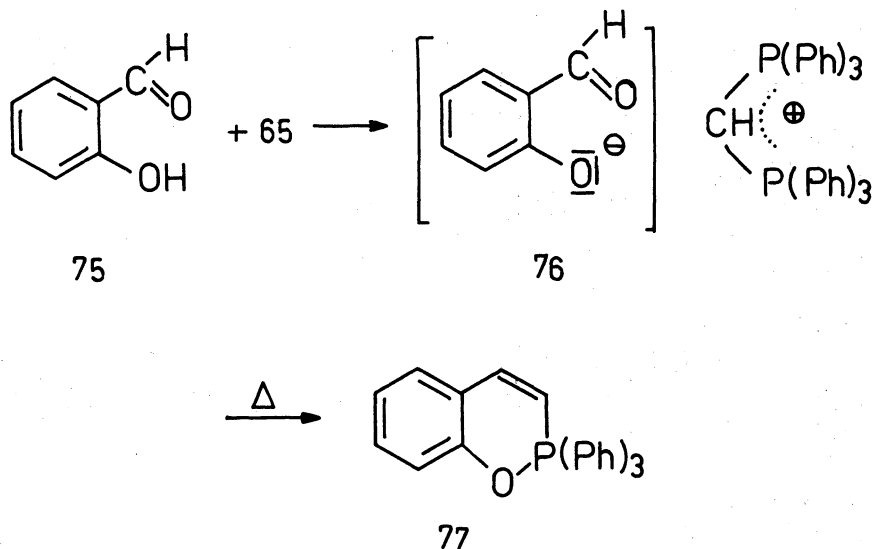
The reaction between (65) and aldehydes leads to products whose structures has
not yet been determined. Salicylaldehyde, (75), reacts with (65) to give
salt (76), which eliminates phosphine oxide on heating to give Benzo-p^5-
oxaphosphorine, (77).[43]
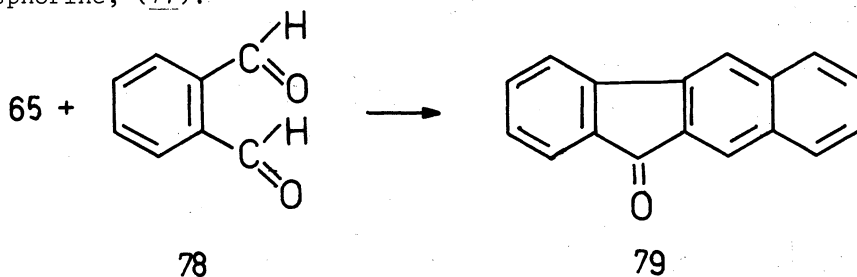
Benzofluorenone (79) results from an, as yet, unexplained reaction between
(65) and orthophtaldialhehyde, (78).[44]

(65) can be reacted with a multitude of organic haolgen compounds.[45] With
methyl iodide, (80), the salt (81) is formed. The action of base on (81)
leads to the elimination of a proton from the position ß to the P-atom. The
zwitterionic molecule (82) does not, however, as may be expected from the
known ß-elimination of phosphonium salts,[46] lose triphenylphosphine, but
rearranges to (84), for which rearrangement the intermediate (83) has been
postulated.[45]

$$65 + CH_3J \longrightarrow \left[CH_3 - C \begin{matrix} \nearrow P(Ph)_3 \\ \oplus \\ \searrow P(Ph)_3 \end{matrix} \right] J^{\ominus} \xrightarrow{\text{Base}}$$

$$80 \qquad\qquad\qquad\qquad\qquad 81$$

$$\overset{\ominus}{I}CH_2 - C \begin{matrix} \nearrow P(P)_3 \\ \oplus \\ \searrow P(P)_3 \end{matrix} \longrightarrow (Ph)_3 \overset{\oplus}{P} - \overset{\ominus}{\underset{|}{C}} - P \begin{matrix} CH_2 \\ | \\ \cdots Ph \\ \searrow Ph \end{matrix}$$

$$82 \qquad\qquad\qquad\qquad 83 \quad Ph$$

$$\longrightarrow (Ph)_3 \overset{\oplus}{P} - \overset{\ominus}{\underset{\underset{Ph}{|}}{C}} - CH_2 - P(Ph)_2 \qquad 84$$

(65) reacts with allyl bromide (85) to give salt (86). With base the betain
(87) is formed, which then cyclises to the crystalline, isolable P^5-pholene
ylid, (88).[45]

$$65 + Br - CH_2 - CH = CH_2 \longrightarrow$$

$$85$$

$$\left[CH_2 = CH - CH_2 - C \begin{matrix} \nearrow P(Ph)_3 \\ \oplus \\ \searrow P(Ph)_3 \end{matrix} \right] Br^{\ominus} \xrightarrow{\text{Base}}$$

$$86$$

$$CH_2 = CH - \underset{\ominus}{CH} - C \begin{matrix} \nearrow P(Ph)_3 \\ \oplus \\ \searrow P(Ph)_3 \end{matrix} \longrightarrow$$

$$87$$

$$88$$
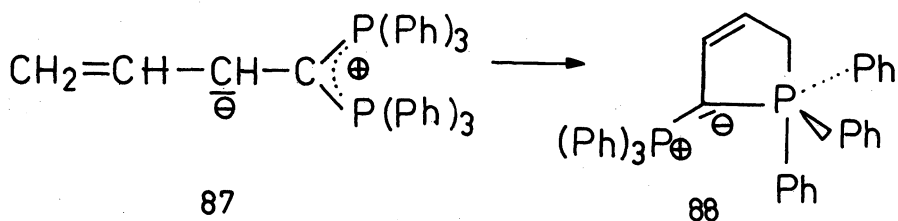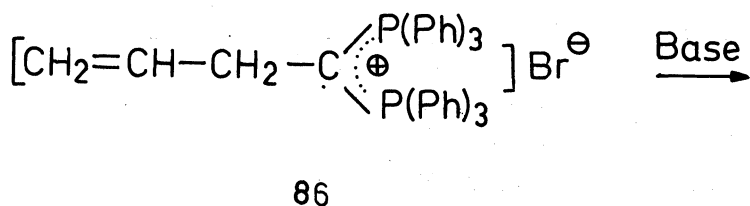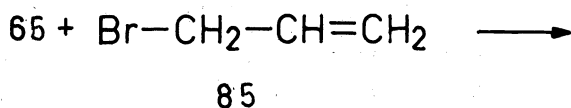
25 years have passed since the discovery of the Wittig reaction, but the
multitude of possible reactions of phosphorus ylids have still not been
exhaustively investigated. Phosphorus ylids represent a broad and fruitful
field of study for preparative and theoretical chemists both now and in the
future.

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