SYNTHESIS OF UNSATURATED NITRO COMPOUNDS
WITH THE AID OF TRIPHENYLPHOSPHINE

COMMUNICATION 1. REACTION OF METHYL (TRIPHENYLPHOSPHORANYLIDENE)
ACETATE WITH AROMATIC NITRO ALDEHYDES

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
No. 4, pp. 673-677, April, 1960
Original article submitted July 30, 1958

In 1919-20 Staudinger and Meyer [1] described the preparation of the phenylamine of diphenylketene from
(diphenylmethylene) triphenylphosphorane and phenyl isocyanate by heating a mixture of them in benzene.
They considered that the reaction can be expressed by the scheme:

\[
\text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{C} (\text{C}_6\text{H}_5)\text{C} + \text{C}_6\text{H}_5\text{NCO} \rightarrow \text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{C} (\text{C}_6\text{H}_5)\text{C} \]

\[
\quad \text{O} \text{C} \text{NC}_6\text{H}_5
\]

\[
\rightarrow \text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{C} = \text{NC}_6\text{H}_5 + \text{(C}_6\text{H}_5\text{)}_3\text{PO}\
\]

A little later Luscher [2] carried out the reaction of (diphenylmethylene) triphenylphosphorane with diphenylketene
and obtained tetraphenylallene:

\[
\text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{C} (\text{C}_6\text{H}_5)\text{C} + \text{(C}_6\text{H}_5)\text{C} = \text{O} \rightarrow \text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{C} = \text{C} (\text{C}_6\text{H}_5)\text{C} + \text{(C}_6\text{H}_5\text{)}_3\text{PO}\
\]

From 1953 onward there appeared a series of papers by Wittig [3, 4] in which methylenephosphoranes were
used as reagents for the introduction of a double bond into various organic compounds:

\[
\text{(C}_6\text{H}_5\text{)}_3\text{P} + \text{XCH}_2\text{R} \rightarrow \text{(C}_6\text{H}_5\text{)}_3\text{P} \cdot \text{XCH}_2\text{R} \rightarrow \text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{C} = \text{CHR} \]

\[
\text{X} = \text{Cl, Br}
\]

\[
\text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{C} = \text{CHR} + \text{R'} \text{COR''} \rightarrow \text{R' = C = CHR} + \text{(C}_6\text{H}_5\text{)}_3\text{PO}\
\]

Taking the reaction between methylenetriphenylphosphorane as their example, Wittig and Schöllkopf [4]
proposed the following mechanism for this peculiar reaction: the betaine analog is first formed,

\[
\text{(C}_6\text{H}_5\text{)}_3\text{P} = \text{CH}_2 + \text{(C}_6\text{H}_5\text{)}_3\text{CO} \rightarrow \text{(C}_6\text{H}_5\text{)}_3\text{P} \text{CH}_2 \text{C} \text{(C}_6\text{H}_5\text{)}_3\text{O}\
\]

and this, as a result of the tendency for phosphorus to form a decet, is converted into an intermediary having a
four-membered ring:
This decomposes into triphenylphosphine oxide and 1,1-diphenylethylene:

The formation of betaine analogs in this reaction was confirmed by the formation of a crystalline salt by treatment of the "betaine" (arising in the reaction between methylenetriphenylphosphorane and benzaldehyde) with HBr and the reverse transformation of this salt into the original betaines when treated with RLi:

This reaction is remarkable in that the corresponding unsaturated compounds can be prepared from many aldehydes and ketones without any effect on other functional groups. This reaction interested us because of the possibility of preparing unsaturated nitro compounds in this way.

Only one example of such a reaction is given in the previous papers on this subject: the preparation of 1-p-nitrophenyl-1-phenylethylene from 4-nitrobenzophenone and methylenetriphenylphosphorane [4]:

In the present paper we describe the reaction of some aromatic nitro aldehydes with methyl (triphenylphosphoranylidene) acetate \((\text{C}_6\text{H}_5)_3\text{P}=\text{CHCOOCH}_3\) (I). We carried out the reaction of methyl (triphenylphosphoranylidene) acetate with o-nitrobenzaldehyde, m-nitrobenzaldehyde, p-nitrobenzaldehyde, o-nitrocinnamaldehyde, and 2,4,6-trinitrobenzaldehyde:

\[
\text{NO}_2-\begin{array}{c}
\text{CH}=\text{CHO}\\(\text{C}_6\text{H}_5)_3\text{P}=\text{CHCOOCH}_3
\end{array} \rightarrow \text{NO}_2-\begin{array}{c}
\text{CH}=\text{CHCOOCH}_3
\end{array}
\]

(I)

\[
\text{O}_2\text{N}-\begin{array}{c}
\text{CH}=\text{CHO}\\(\text{C}_6\text{H}_5)_3\text{P}=\text{CHCOOCH}_3
\end{array} \rightarrow \text{O}_2\text{N}-\begin{array}{c}
\text{CH}=\text{CHCOOCH}_3
\end{array}
\]

(II)

\[
\text{O}_2\text{N}-\begin{array}{c}
\text{CH}=\text{CHO}\\(\text{C}_6\text{H}_5)_3\text{P}=\text{CHCOOCH}_3
\end{array} \rightarrow \text{O}_2\text{N}-\begin{array}{c}
\text{CH}=\text{CHCOOCH}_3
\end{array}
\]

(III)

\[
\text{O}_2\text{N}-\begin{array}{c}
\text{CH}=\text{CHCHO}\\(\text{C}_6\text{H}_5)_3\text{P}=\text{CHCOOCH}_3
\end{array} \rightarrow \text{O}_2\text{N}-\begin{array}{c}
\text{CH}=\text{CHCH}=\text{CHCOOCH}_3
\end{array}
\]

(IV)

\[
\text{NO}_2-\begin{array}{c}
\text{CH}=\text{CHCHO}\\(\text{C}_6\text{H}_5)_3\text{P}=\text{CHCOOCH}_3
\end{array} \rightarrow \text{NO}_2-\begin{array}{c}
\text{CH}=\text{CHCH}=\text{CHCOOCH}_3
\end{array}
\]

(V)