Tetrahedron Letters No.1, pp. 85-89, 1968. Pergamon Press Ltd. Printed in Great Britain.

TRIPHENYLDIETHOXYPHOSPHORANE AND
TRIBUTYLDIETHOXYPHOSPHORANE.[1]

Donald B. Denney, Dorothy Z. Denney and Louis A. Wilson

School of Chemistry
Rutgers, The State University
New Brunswick, N. J., 08903

(Received in USA 16 August 1967)

Horner and Jurgeleit[2] showed that diethyl peroxide reacts with trisubstituted phosphines to give the phosphine oxides. Previous work from this laboratory[3] has shown that intermediates are involved in the reactions, however, it was not possible to distinguish between a diethoxyphosphorane (I) or the alkoxyphosphonium alkoxide ion pair

$$\underset{\text{I}}{R_3P(O\text{-}C_2H_5)_2} \rightleftarrows \underset{\text{II}}{R_3\overset{+}{P}\text{-}O\text{-}C_2H_5 + C_2H_5O^-}$$

(II) or an equilibrium mixture of the two. In the case of trisubstituted phosphites it was shown that pentaalkoxyphosphoranes are formed as stable products.[4]

Triphenyphosphine in benzene (^{31}P + 6 ppm relative to 85% phosphoric acid)[5] reacts with diethyl peroxide to give after 5 hr. a solution whose ^{31}P nmr spectrum shows absorptions at -26 ppm, triphenylphosphine oxide, +6 ppm and +55 ppm. During the period of one week the -26 and +55 ppm absorptions grow at the expense of the +6 ppm absorption. The experiment was repeated in methylene chloride with a different sample of diethyl peroxide. After six days the ^{31}P nmr spectrum showed a very weak absorption at -28 ppm, a fairly strong absorption at +5 ppm with the major absorption at +54 ppm.

The same reactants in methylene chloride ethanol (2:1) gave mainly triphenylphosphine oxide (-28 ppm); absorptions were also present at +5 and +54 ppm.

The ^{1}H nmr spectrum of the reactants in benzene after 5 hr shows a quintet at 2.7 ppm (relative to tetramethylsilane). This is typical of the CH_2 hydrogens of $P\text{-}O\text{-}CH_2\text{-}CH_3$ where J_{HH} = 7 cps and J_{PH} = 7 cps. A triplet was also found at 0.8 ppm (J = 7 cps). The spectrum also included absorptions for diethyl peroxide. A reaction mixture in methylene chloride showed a similar pattern, quintet at 2.6 ppm (J_{HH} = 7 cps, J_{PH} = 7 cps) and a triplet at 0.75 ppm (J = 7 cps).

Benzoic acid was added to a reaction mixture of triphenylphosphine and diethyl peroxide in benzene 7 days after mixing; an exothermic reaction took place. Triphenylphosphine oxide formed and the +55 material disappeared completely. The quintet and triplet also disappeared from the ^{1}H nmr spectrum. Ethyl benzoate was formed as evidenced by nmr and glpc analysis.

The results of these experiments indicate that triphenylphosphine and diethyl peroxide react to form triphenyldiethoxyphosphorane (III). This is the material which absorbs at +54.5 ± 1 ppm and which reacts

$$(C_6H_5)_3P(O\text{-}C_2H_5)_2 \qquad (C_6H_5)_3\overset{+}{P}\text{-}O\text{-}C_2H_5 + \overset{-}{BF_4}$$

$$^{31}P \;\; +54 \text{ ppm} \qquad\qquad ^{31}P \;\; -62 \text{ ppm}$$

$$\text{III} \qquad\qquad\qquad\qquad \text{IV}$$

with benzoic acid to give ethyl benzoate, triphenylphosphine oxide and ethanol. This phosphorane is fairly stable; heating a benzene solution at 60° for ca. 10 hr did not lead to appreciable conversion to triphenylphosphine oxide. It has not been possible to isolate the pure phosphorane as yet.

The alternate formulation of this material as triphenylethoxyphosphonium ethoxide seems unreasonable because alkylation of triphenylphosphine oxide with triethyloxonium fluoroborate in methylene chloride yields a material with ^{31}P absorption at -62 ppm. The ^{1}H nmr spectrum had a quintet at 4.4 ppm (J_{HH} = 7 cps; J_{PH} = 7 cps). The methyl region was complicated by absorptions for ether and triethyloxonium fluoroborate. This material is undoubtedly triphenylethoxyphosphonium fluoroborate (IV).

Tributylphosphine and diethyl peroxide were allowed to react neat at room temperature. After 1 hr the ^{31}P nmr spectrum showed an absorption at -44 ppm, tributylphosphine oxide, +33 ppm, tributylphosphine and another absorption at +38 ppm. The +38 ppm absorption was considerably larger than the -44 ppm absorption. After 1 day the major absorption appeared at -44 ppm; essentially no tributylphosphine remained. The material with the +38 ppm absorption was still present however the amount was small relative to tributylphosphine oxide. A weak absorption was present at -54 ppm. This might be due to $(C_4H_9)_2P(O)O\text{-}C_4H_9$. Compounds of this structure absorb at -54.9 ppm. The ^{1}H nmr spectrum was followed during the course of the reaction. The disappearance of diethyl peroxide could be observed. After completion of the reaction ethanol, diethyl ether and tributylphosphine oxide were present as the major products as evidenced by nmr and glpc. At no time during the reaction did a pattern develop in the $-CH_2-$ region of the nmr spectrum which is typical of $P\text{-}O\text{-}CH_2CH_3$. It should be noted that this region is quite complex because ethanol and diethyl ether are being formed continuously and thus a detailed interpretation will require a very thorough study.

In another experiment an equimolar reaction mixture of tributylphosphine and diethyl peroxide was treated with excess benzoic acid 7 hr after mixing. An exothermic reaction occurred. The +38 ppm peak in the ^{31}P nmr spectrum disappeared and the tributylphosphine oxide absorption increased in intensity. Glpc analysis of the reaction mixture showed that ethyl benzoate was formed. These data suggest that the initial reaction product is tributyldiethoxyphosphorane (V) and that this decomposed fairly rapidly.

$(C_4H_9)_3P(O\text{-}C_2H_5)_2$	$(C_4H_9)_3\overset{+}{P}\text{-}O\text{-}C_2H_5 + BF_4^-$
^{31}P +38 ppm	^{31}P -98 ppm
V	VI

The detailed structure of this material is not as clear as that of III because coupling of the CH_2 of the ethoxy group to phosphorus could not be established. It does appear though that the material is not tributylethoxyphosphonium ethoxide. Alkylation of tributylphosphine oxide with triethyloxonium fluoroborate in methylene chloride gave VI whose ^{31}P nmr spectrum showed an absorption at -98 ppm. The ^{1}H nmr spectrum showed a quintet at 4.3 ppm (J_{HH} = 7 cps; J_{PH} = 7 cps). These data indicate that the tributylphosphine-diethyl peroxide product is more closely represented by the structure V, however, it may be in equilibrium with a small amount of the phosphonium salt. If the equilibration is rapid enough then $P\text{-}O\text{-}CH_2$ coupling would not be observed.

The results of these experiments point to the value of the diethyl peroxide-trivalent phosphorus compound reaction as a general route to pentasubstituted phosphorus compounds. They also show that triaryl and trialkyldialkoxyphosphoranes are reasonably stable materials and thus the study of their chemistry and of related materials is now possible.

REFERENCES

1. This research has been supported by the National Science Foundation under NSF GP 4997X and by the National Institutes of Health under GM-12625.

2. L. Horner and W. Jungeleit, Ann., **591**, 138 (1955).

3. (a) D.B. Denney, H.M. Relles and A.K. Tsolis, J. Am. Chem. Soc. **86**, 4487 (1964); (b) D.B. Denney and N.G. Adin, Tetrahedron Letters, No. 23, 2569 (1966).

4. (a) D.B. Denney and H.M. Relles, J. Am. Chem. Soc., **86**, 3897 (1964); (b) D.B. Denney and S.T.D. Gough, ibid., **87** 138 (1965); (c) D.B. Denney and L. Saferstein, ibid., **88**, 1830 (1966).

5. All ^{31}P nmr spectra were recorded with a Varian Associates HA-100 operating at 40.5 MHz.