of 195° (see Table I). The ir [3500 (OH), 1710 cm^{-1} ($C{=}O$)] and nmr [δ 3.43 (1, b, OH), 3.00 (1, m, $-COCH<$, $J = 7$ Hz), 1.27 (6, s, $-C(OH)(CH_3)_2$), 1.04 (6, d, $-CH(CH_3)_2$, $J = 7$ Hz] were in agreement with the values previously published.[27]

2-Acetoxy-2,4-dimethyl-3-pentanone (4-OAc). Keto ester **4**-OAc was collected by preparative glpc using a column temperature of 195° (see Table I): ir 1744 and 1723 ($C{=}O$), 1252 cm^{-1}; nmr δ 2.90 (1, h, $-COCH<$, $J = 7$ Hz), 2.01 (3, s, $-O_2CCH_3$), 1.43 (6, s, $-C(OCOCH_3)(CH_3)_2$), 1.03 (6, d, $-COCH(CH_3)_2$, $J = 7$ Hz); mass spectrum *m/e* 172 $[M]^+$, 129 $[(CH_3)_2CHCOC(CH_3)_2O]^+$ and/or $[CH_3CO_2C(CH_3)_2C{\equiv}O]^+$, 101 $[CH_3CO_2C(CH_3)_2]^+$, 71 $[(CH_3)_2CHC{\equiv}O]^+$, 59 $[CH_3CO_2]^+$, 43 $[(CH_3)_2CH]^+$, and/or $[CH_3C{\equiv}O]^+$. The ir and nmr values were in agreement with values previously reported in the literature.[15b]

Anal. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.37. Found: C, 62.7; H, 9.30.

1-(2-Furanyl)-2,4-dimethyl-3-pentanone (10). Adduct **10** was collected using preparative glpc, column temperature 190°. From the ir [1715 ($C{=}O$), 1145 cm^{-1} (COC)], nmr [δ 7.23 (1, m, α-H of furan), 6.17, 5.90 (2, m, β-H of furan), 3.17–2.27 (4, m, $-CH_2CH<$, $HCCO-$, $-COCH$), 1.05, 1.02, 0.90 (9, three overlapping doublets, CH_3-, $J = 7$ Hz)], and mass spectra {*m/e* 180 $[M]^+$, 137 $[C_4H_3OCH_2CH(CH_3)C{\equiv}O]^+$, 109 $[C_4H_3OCH_2CH(CH_3)]^+$, 81 $[C_4H_3OCH_2]^+$, 71 $[(CH_3)_2CHC{\equiv}O]^+$, 43 $[(CH_3)_2CH]^+$}, structure **10** is assigned to this compound.

2,2,4,4-Tetramethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (9). Cycloadduct **9** was collected by preparative glpc using a column temperature of 190° (see Table I): ir 1710 ($C{=}O$), 1380, 1065, 920 cm^{-1}; nmr 6.27 (2, s, $=CH$), 4.27 (2, s, $>CH$), 1.30 (6, s, CH_3), 0.88 (6, s, CH_3). The ir and nmr are in agreement with those previously reported,[12a] with the exception that ir bands at 805 and 735 cm^{-1} were not observed.

2,4-Dimethyl-3-pentanone (7). Saturated ketone **7** was isolated (for example, 43%, Table II, entry 4) by distillation of the reaction mixture at atmospheric pressure (bath temperature, 125–160°): ir 1710 cm^{-1} ($C{=}O$); nmr δ 2.63 (2, h, $(CH_3)_2CH-$, $J = 7$ Hz), 0.93 (12, d, CH_3, $J = 7$ Hz). The ir, nmr, and glpc were identical with those of an authentic sample.

1,3-Dibenzoyloxy-2-propanone (22). Keto diester **22** was obtained by crystallization of the crude reaction mixture (see Table III, entry 1), using ether–pentane: mp 119° (lit.[34] mp 118–119°); ir 1735 cm^{-1} ($C{=}O$); nmr δ 8.2 (4, b, *o*-CH), 7.6 (6, b, *m*-, *p*-CH), 5.11 (4, s, CH_2). The filtrate from crystallization of **22** was concentrated and distilled in vacuum, to give **4**-OCOPh: ir 1735 cm^{-1} ($C{=}O$) (lit.[35] 1725 cm^{-1}); nmr δ 8.0 (2, b, *o*-CH), 7.5 (3, b, *m*-,*p*-CH), 4.77 (2, s, CH_2), 2.19 (3, s, CH_3). The ratio of mono- to dibenzoate could be calculated directly from an nmr of the crude reaction mixture (see Table III).

Acknowledgments. Partial support for this research by the Swedish Natural Science Research Council is gratefully acknowledged. One of us (J. C.) is indebted to the Petroleum Research Fund of the American Chemical Society and to the Committee for the International Exchange of Persons (Fulbright-Hayes).

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Preparation and Chemistry of Some Cyclic Phosphoranes[1]

D. B. Denney,* D. Z. Denney, C. D. Hall,[2] and K. L. Marsi[3]

Contribution from the School of Chemistry, Rutgers University,
New Brunswick, New Jersey 08903. *Received March 13, 1971*

Abstract: The reactions of the phosphines **1**–**8** with diethyl peroxide have been studied. The products from **1** and **2** have the properties of pentasubstituted phosphorus compounds **9** and **10**. The products from **4** and **5** consist of equilibrium mixtures of pentasubstituted phosphorus compounds and alkoxyphosphonium alkoxides. The product from **7** undergoes reverse cycloaddition to isoprene and diethyl phenylphosphonite. The product from **8** rearranges to that from **7**. The relative rates of reaction of the phosphines with diethyl peroxide in cyclopentane are **1**, 3.8, **6**, 2.0, **4**, 1.3, and **3**, 1.0; in methylene chloride the relative rates are **1**, 3.1, **6**, 1.7, **4**, 1.6, and **3**, 1.0. The relative rates of reaction of the phosphines with ethyl iodide in acetonitrile are **4**, 1.5, **3**, 1.0, **6**, 0.9, and **1**, 0.33. The rate orders for these two reactions are the reverse of each other. The rate order for the diethyl peroxide reaction supports the concept of this being a biphilic displacement process in which the phosphorus atom is bonding to both oxygens in the transition state of the rate-controlling step.

In earlier work it was shown that a wide variety of trisubstituted phosphorus compounds react with diethyl peroxide to give the appropriate pentasubstituted phosphorus compound.[4,5] In particular, a series of cyclic and acyclic phosphites was shown to give phosphoranes, as were acyclic phosphines. In the present study a variety of cyclic phosphines have been allowed to react with diethyl peroxide. The aims of this investigation were to continue to test the peroxide route as a method of preparing phosphoranes, to learn more about the mechanism of the reaction, and to investigate the chemistry of the products of these reactions. The reactions of diethyl peroxide with trisubstituted phosphorus compounds usually yield the pentasubstituted material which is contaminated with varying amounts of tetrasubstituted material, *e.g.*, phosphate, phosphine oxide, etc. In general it has not been possible to purify the pentasubstituted materials to the point where good analytical data can be obtained. Similarly, attempts to observe a parent molecular ion by mass spectrometry have been fruitless, with the compounds being reported here. The structural assignments have been made on the basis of ^1H and ^{31}P nmr spectroscopy, method of

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(2) On leave from the Chemistry Department, King's College, University of London.

(3) Special Postdoctoral Fellow of the National Institutes of Health, 1967–1968, on leave from the Chemistry Department of Long Beach State College.

(4) D. B. Denney and D. H. Jones, *J. Amer. Chem. Soc.*, 91, 5821 (1969).

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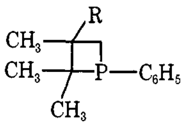
preparation, and reactions of the pentasubstituted materials.

Results

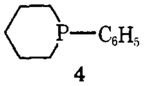
The compounds **1**–**8** were allowed to react with diethyl peroxide. In the case of **1** and **2** the reactions proceeded rapidly to give materials whose ^{31}P chemical shifts were +36.[6] These values are more positive than those of the starting phosphines and they provide strong evidence for the formation of pentasubstituted phosphorus compounds **9** and **10**.[7,8] **9** was also formed by alkylating the corresponding phosphine oxide with triethyloxonium fluoroborate[9] to give the salt **11**, which reacted with ethoxide ion to produce **9**. The latter sequence is not a general one for the preparation of phosphoranes.



1, R = CH_3
2, R = H

C_6H_5—$P(CH_3)_2$

3



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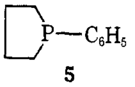
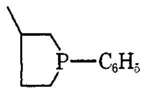
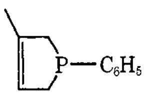


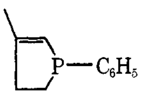
5



6, cis and trans

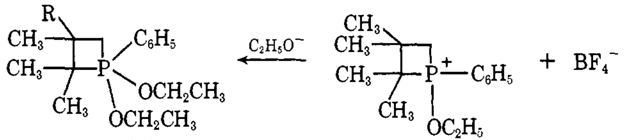


7



8

1 or 2 + $(C_2H_5O)_2$ ⟶



9, R = CH_3
10, R = H

11

The variable-temperature ^1H nmr spectra of **9** and the related phosphorane in which four methyl groups occupy the positions α to phosphorus have been studied in detail and they have been interpreted in terms of pseudorotation processes.[10]

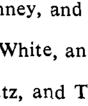
The compounds **4** and **5** reacted with diethyl peroxide to give new substances **12** and **13** which showed ^{31}P absorptions at +48 and +12, respectively. The proton nmr spectrum of **12** in methylene chloride at 32° shows a triplet for the absorption of the methyl group hydrogens of the ethoxy groups at 0.87 (J_{HH} = 7 Hz). The absorption of the hydrogens of the methylene group of the ethoxy groups is found as a broad quartet, 2.7–3.0. At −60° the triplet has broadened and is now found at 0.79. The absorption of the methylene group hydrogens is now a broad quintet, 2.49–2.94. In chlorobenzene at 30°, **12** shows a broad triplet at 0.82 (J_{HH} = 7 Hz) and the absorption of the methylene group hydrogens is found as a "mound" centered at 2.80. At 100° the triplet is sharp, 0.87, and the absorption of the methylene group hydrogens is now found as an asymmetric quartet.

The methyl group hydrogens of the ethoxy groups of **13** (methylene chloride) absorb at 0.87 as a broad triplet (J_{HH} = 7 Hz). The methylene group hydrogens show an absorption at 2.88 which is quintet like. The spectrum at −60° has a broad triplet at 0.81 and a broad quintet at 2.66. In chlorobenzene the methyl group hydrogens absorb as a sharp triplet at 0.88 and the methylene group hydrogens are found as a sharp quintet at 2.97 (J_{PH} = J_{HH} = 7 Hz). At 100° the quintet has broadened and is found at 3.10. The triplet is still sharp, 0.92. Changes in the patterns of the absorptions of the ring hydrogens of both **12** and **13** were noted with the changes in conditions; however, no interpretable absorptions emerged.

Compound **6** reacted with diethyl peroxide to give a compound which absorbed at +11.5 in the ^{31}P nmr spectrum. This material was not investigated in detail.

8 was prepared from isoprene and phenyldichlorophosphine followed by hydrolysis and reduction of the oxide with trichlorosilane. This procedure yields mainly **8** contaminated with a few per cent of **7**.[11] The reaction of **8** plus a small amount of **7** took an interesting course in that diethyl phenylphosphonite and isoprene were the major products.

8 + $(C_2H_5O)_2$ ⟶



+ $C_6H_5P(OC_2H_5)_2$

In order to learn more about the diethyl peroxide trisubstituted phosphorus compound reaction, the relative rates of reaction of **1**, **3**, **4**, and **6** were measured in cyclopentane and methylene chloride and compared to the relative rates of reaction of the same phosphines with ethyl iodide in acetonitrile. The relative rate data were

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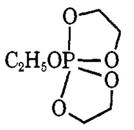
[6] All ^{31}P chemical shifts are reported in parts per million using 85% phosphoric acid as 0 ppm.

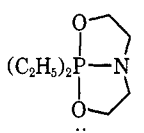
[7] F. Ramirez, *Bull. Soc. Chim. Fr.*, 3491 (1970).

[8] The assignment of structure of the reaction products of trivalent phosphorus compounds with diethyl peroxide has rested in the main on their ^{31}P and ^1H nmr spectral data as well as their conversion to ethyl benzoate and the appropriate phosphoryl compound on treatment with benzoic acid. The major difficulty associated with the isolation and purification of these materials has been their hydrolytic and thermal instability as well as the fact that their preparation usually leads to some oxide. The data outlined above strongly support the assigned structures; however, the data are not of the traditional type and therefore further structural proof is welcome.

A mixture of pentaethoxyphosphorane (1 mol) and ethylene glycol (2 mol) was evaporatively distilled under reduced pressure to provide a material, i, whose spectral data agree with those found for the material in solution. This material was analyzed. *Anal.* Calcd for $C_6H_{13}O_5P$: C, 36.74; H, 6.68. Found: C, 36.64; H, 6.76.



i



ii

Exchange of a reaction mixture containing diphenyltriethoxyphosphorane with diethanolamine followed by evaporative distillation yielded a material, ii, whose spectral properties were in agreement with those assigned by the solution spectra. *Anal.* Calcd for $C_{16}H_{18}O_2NP$: C, 66.89; H, 6.31; N, 4.65. Found: C, 66.72; H, 6.23; N, 4.65. The parent ion in the mass spectrum was found at 287; calcd 287.

These results strongly support the structures assigned to the two compounds, and they further support the general contention that many reactions of trivalent phosphorus compounds with diethyl peroxide yield phosphoranes or equilibrium mixtures of phosphoranes and phosphonium ethoxides. The structural assignments reported in this paper rest in the main on the kind of data obtained by spectral analysis of the reaction mixtures and by chemical reactions. It is hoped that with a greater understanding of these materials they can be characterized more fully.

The results reported above were obtained by Dr. B. C. Chang. The analyses were by G. Robertson and the mass spectrum was obtained by Dr. M. Schulmann.

[9] J. H. Finley, D. Z. Denney, and D. B. Denney, *J. Amer. Chem. Soc.*, 91, 5826 (1969).

[10] D. Z. Denney, D. H. White, and D. B. Denney, *ibid.*, 93, 2066 (1971).

[11] L. D. Quin, J. P. Gratz, and T. P. Barket, *J. Org. Chem.*, 33, 1034 (1968).

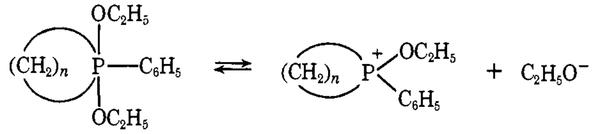
obtained by allowing an equimolar mixture of **3** and another phosphine to react with 0.5 equiv of ethyl iodide and by allowing **6** and another phosphine to react with 0.5 equiv of diethyl peroxide. The course of the reactions was followed by ^{31}P nmr spectroscopy and the final ratio of products and starting materials was obtained by area measurements in the reactions of ethyl iodide and in the reaction of diethyl peroxide in cyclopentane. Peak height measurements were used for the reactions of diethyl peroxide in methylene chloride and they may be less reliable. Half-life measurements were made for the reactions of **3** and **4** with diethyl peroxide in cyclopentane and acetonitrile.

The results of the above experiments can be summarized as follows: the relative rates for the ethyl iodide reactions are **4**, 1.5, **3**, 1.0, **6**, 0.9, and **1**, 0.33; the relative rates for the diethyl peroxide reaction in cyclopentane are **1**, 3.8, **6**, 2.0, **4**, 1.3, and **3**, 1.0; in methylene chloride the relative rates are **1**, 3.1, **6**, 1.7, **4**, 1.6, and **3**, 1.0. The half-lives for the reactions of **3** with diethyl peroxide in cyclopentane and acetonitrile were found to be 4.2 and 3.7 hr, respectively, and for **4**, 2.75 and 1.5 hr.

During the course of these and other studies it has been noted that high yields of phosphoranes can be obtained from the diethyl peroxide reaction if careful attention is paid to the purity of the starting materials and solvents. In particular there appears to be some advantage in using cyclopentane as a solvent.

Discussion

In earlier work it was noted that the products of the reactions of diethyl peroxide with trisubstituted phosphorus compounds sometimes showed coupling of the methylene group hydrogens of the ethoxy groups to phosphorus and in some cases such coupling was not found.[5] Lack of coupling was attributed to rapid ionization of the pentasubstituted phosphorus compound to phosphonium ethoxide ion pairs. It was also found that the presence or absence of coupling was temperature and solvent dependent. Similar behavior has been noted by Ramirez and coworkers with cyclic five-membered ring phosphoranes which have nitrogen bonded to phosphorus.[12] The ^{1}H nmr spectral data for compounds **12** and **13** are also explained by the ionization hypothesis; thus **12** shows an ^{1}H nmr temperature dependence in methylene chloride which indicates that ionization has been slowed on the nmr time scale at −60° to the extent that phosphorus–hydrogen coupling is observable. Ionization is not as facile in chlorobenzene and loss of coupling is observed at elevated temperatures.



12, $n = 5$
13, $n = 4$

Compound **13** apparently does not ionize as readily as **12** or diethoxydimethylphenylphosphorane[5] and some coupling of the methylene group hydrogens is present in methylene chloride solution. Ease of ionization appears to be a function of ring size in the order 6 > 5 > 4. There is no evidence for ionization on the nmr time scale with **9** or **10**. The order may be associated with an increase in strain in proceeding from a pentacoordinate to a tetracoordinate structure. This is most easily seen in considering the transformation of **11** to **9**. In **11** the ring is strained because of the tetrahedral nature of phosphorus. In **9** the ring should be much less strained as long as the two carbon–phosphorus bonds occupy an equatorial and an apical position in the trigonal-bipyramidal structure. Trigonal-bipyramidal structures are usually assumed for pentasubstituted phosphorus compounds in solution and they are definitely found in the solid state.[13] Ring strain effects in pentasubstituted phosphorus compounds have been noted by several investigators.[14] It is not clear just how much ring strain is associated with a five-membered ring compound such as **13**. Muetterties and coworkers[14a] showed that the trifluoro five-membered ring containing phosphorane analogous to **13** is undergoing pseudorotation at room temperature and that inhibition of pseudorotation occurs at lower temperatures with the favored structure being that in which the ring takes up two equatorial positions. Ionization complicates such a structural analysis for **12** and **13**. It may be that neither undergoes pseudorotation; however, no definitive statement can be made at this time. It should be noted that pseudorotation has been implicated in the hydrolyses of five- and six-membered ring phosphonium salts in which phosphorus is one atom of the rings.[15]

The reactions of **7** and **8** with diethyl peroxide undoubtedly form phosphoranes **14** and **15**. Decomposition of **14** by reverse cycloaddition yields isoprene and diethyl phenylphosphonite. The addition of phosphites to dienes to give phosphoranes has been observed.[16] In general the phosphites have contained a five-membered ring, a factor which undoubtedly stabilizes the phosphorane. Lack of the ring apparently favors reversal of the cycloaddition reaction. Conversion of **15** into **14** *via* ionization and tautomeric hydrogen shift can account for the production of isoprene and diethyl phenylphosphonite from **8** and diethyl peroxide.

In an earlier paper[4] the mechanism of the peroxide-trisubstituted phosphorus compound reaction was discussed in terms of two extreme possibilities (1) and (2). The first envisions direct formation of the pentasubstituted phosphorus compound by a biphilic displacement reaction, *i.e.* the trisubstituted phosphorus compound behaves as a biphile in that it exhibits both nucleophilic and electrophilic properties in the rate-con-

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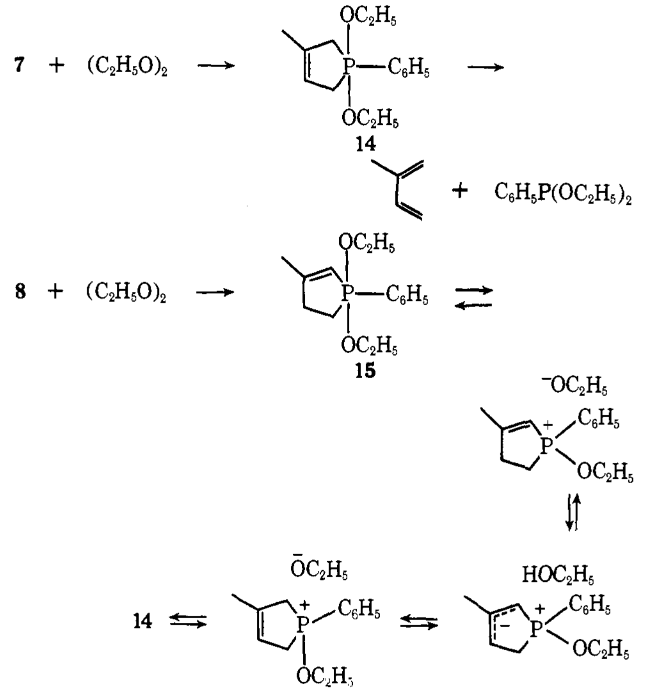
(12) (a) F. Ramirez, A. U. Patwardhan, H. J. Kugler, and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 6276 (1967); (b) F. Ramirez, A. S. Gulati, and C. P. Smith, *ibid.*, **89**, 6283 (1967); (c) F. Ramirez, J. F. Pilot, and C. P. Smith, *Tetrahedron*, 24, 3735 (1968); (d) F. Ramirez, A. U. Patwardhan, H. J. Kugler, and C. P. Smith, *ibid.*, 24, 2275 (1968).

(13) (a) W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 2268 (1969); (b) R. D. Spratley, W. C. Hamilton, and J. Ladell, *ibid.*, **89**, 2272 (1967).

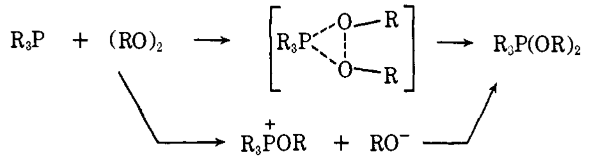
(14) (a) E L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); (b) D. Gorenstein and F. H. Westheimer, *J. Amer. Chem. Soc.*, **92**, 634 (1970); (c) E. A. Dennis and F. H. Westheimer, *ibid.*, **88**, 3432 (1966); (d) P. C. Haake and F. H. Westheimer, *ibid.*, **83**, 1102 (1961); (e) D. Gorenstein, *ibid.*, **92**, 644 (1970); (f) G. O. Doak and R. Schmutzler, *Chem. Commun.*, 476 (1970); (g) F. Ramirez, *Accounts Chem. Res.*, 1, 168 (1968); (h) D. Houalla, R. Wolf, D. Gagnaire, and J. B. Robert, *Chem. Commun.*, 443 (1969).

(15) (a) K. L. Marsi and R. T. Clark, *J. Amer. Chem. Soc.*, **92**, 3791 (1970); (b) K. L. Marsi, *ibid.*, **91**, 4724 (1969); (c) W. Egan, G. Chauviere, K. Mislow, R. T. Clark, and K. L. Marsi, *Chem. Commun.*, 733 (1970).

(16) (a) M. Wieber and W. R. Hous, *Tetrahedron Lett.*, 4693 (1969); (b) N. A. Razumova, F. V. Bugrov, and A. H. Petrov, *J. Gen. Chem. USSR*, **39**, 2306 (1969).



trolling step. The general biphilic behavior of trivalent phosphorus compounds has been discussed in some detail by Kirby and Warren.[17] The concept of biphilic displacement reactions has received some recognition.



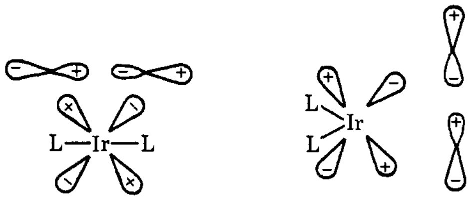
(1)

(2)

Taylor[18] in 1924 showed that phosphorus trichloride and chlorine react in the gas phase to give phosphorus pentachloride. He also showed that the reaction was not subject to wall effects. In a later report Downs and Johnson[19] provided evidence on the basis of tracer experiments which supports a direct formation of phosphorus pentachloride from phosphorus trichloride and chlorine and in which the entering chlorines go into equatorial positions of the forming trigonal bipyramid.

Miller[20] has also recognized that trivalent phosphorus compounds may react with chlorine by a "molecular" mechanism.

More recently Pearson and Muir[21a] have shown that iridium complexes insert into carbon–halogen bonds with complete retention of configuration. They provide evidence that this is a one-step reaction and they have also discussed orbital symmetry requirements for this family of reactions. They point out that a pair of electrons in a d orbital is donated to the σ^* orbital of the C–X bond. The addition can occur in either a cis or trans manner, a and b. Pearson[22] has also discussed such substitutions in a general manner. He points out a filled p orbital as well as a filled d orbital can overlap with a σ^* orbital such as is found in a variety of diatomic molecules, *e.g.*, H_2.

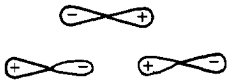


a

b

In the earlier study it was shown that phosphite reactivity toward diethyl peroxide followed the order of stability of the phosphoranes and was opposite to that of various ionic reactions.[4] The kinetic data obtained in this study are of a similar nature in that the rate order for diethyl peroxide is the opposite of that found with ethyl iodide. Clearly caution must be used in interpreting these data because the comparison involves displacement on oxygen in the one case and on carbon in the other; however, the general indications are that two different mechanisms are involved. The biphilic displacement process very adequately accounts for the rate order; in particular, reaction of **1** *via* a transition state in which one α carbon of the ring is entering an equatorial position and the other is entering an apical position of the forming trigonal bipyramid allows a relief of strain in the ring. The negligible solvent effect found on changing from cyclopentane to acetonitrile supports the concept of a transition state for the rate-controlling step which has little or no ionic character.

In terms of orbital symmetry arguments the antibonding orbital, O–O, σ^* must accept a pair of electrons in the same manner as outlined by Pearson and Muir,[21]



c

c. Such an interaction can occur if the electrons are in a d or a p orbital. Recent calculations[23] indicate that the unshared pair of electrons on phosphorus in phosphine and trimethylphosphine is in an orbital with considerable p character. It should also be noted that the oxygen–oxygen bond is very weak, 37 kcal/mol,[24] and thus penetration into the antibonding orbital by the biphile probably does not have to be very great before the transition state is reached. It is important to note that the biphile must have an available orbital to accept a pair of electrons. The biphile exhibits both nucleophilic and electrophilic character. The importance of these contributions will undoubtedly vary with reactants.

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(23) (a) I. H. Hillier and V. R. Saunders, *J. Chem. Soc. A*, 2475 (1970); (b) I. H. Hillier and V. R. Saunders, *Trans. Faraday Soc.*, **66**, 2401 (1970); (c) J. M. Lehn and B. Munsch, *Chem. Commun.*, 1327 (1969).

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Clearly, if these ideas are correct then there should be a family of reactions in which a biphile inserts into a σ bond in one step.

The question should be asked as to why the biphilic displacement reaction may be favored in the reaction of diethyl peroxide and trisubstituted phosphorus compounds. The answer may well be that it is only favored in nonpolar nonhydrogen bonding media. This suggestion arises from the finding that optically active methylpropylphenylphosphine reacted with diethyl peroxide in water–tetrahydrofuran to give methylpropylphenylphosphine oxide with 66% inversion.[25] This result can be most easily explained by an ionic mechanism in which water can stabilize the incipient ethoxide ion in the transition state by hydrogen bonding. This mechanism suggests formation of the intermediate phosphonium salt with complete retention of configuration and hydrolysis should proceed with complete inversion of configuration;[26] there must, therefore, be a competing racemization route. Racemization could arise by the competing biphilic process or by attack of ethoxide ion on the phosphonium ion.

Experimental Section

General. Nmr spectra were obtained on Varian A-60 and HA-100 spectrometers. In particular, low-temperature ^{1}H spectra were recorded with the HA-100. ^{31}P nmr spectra were recorded at 40.5 MHz with 85% phosphoric acid as external standard. Infrared spectra were recorded with an Infracord. Glpc analyses were conducted with an F and M Model 700 gas chromatograph.

Preparation of 1 and 2. These compounds were prepared by the method of Cremer and Chorvat.[27] Their physical properties agreed well with those reported. The ^{31}P nmr spectrum of **1** showed one absorption at −8.5. The compound **2** mixture of cis-trans isomers showed two absorptions at −1.5 and −25.[28]

Reaction of 1 with Diethyl Peroxide. In a representative reaction, 0.9 g (0.01 mol) of diethyl peroxide was added slowly to a stirred solution of 2.06 g (0.01 mol) of **1** in 3 g of methylene chloride at 5°. The mixture was allowed to warm to room temperature and stored in a dessicator. The progress of the reaction was monitored by observing the ^{31}P nmr spectrum of an aliquot. After 48 hr the major absorption was found at +36.

To a portion of this material was added benzoic acid. The ^{31}P nmr spectrum showed that the +36 absorption had disappeared and a new absorption was found at −50 which is identical with that reported for the oxide.

Preparation of 9 by Alkylation of 2,2,3,3-Tetramethyl-1-phenylphosphetane 1-Oxide with Triethyloxonium Fluoroborate Followed by Reaction with Sodium Ethoxide. To 0.93 g (0.0049 mol) of triethyloxonium fluoroborate in 1 g of methylene chloride was added, with stirring, 1.11 g (0.005 mol) of the oxide in 1 g of methylene chloride. The ^{31}P nmr spectrum showed only one absorption at −91.5 which is attributed to **11**.

Most of the volatiles were removed by pumping on the solution at room temperature, and a freshly prepared solution of sodium ethoxide (0.005 mol) in ethanol was added. A heavy white precipitate formed. The mixture was centrifuged and the supernatant liquid showed an absorption at +36 and −51. The first is attributed to **9** and the second to oxide. The ^{1}H nmr spectrum showed absorptions for **9** and oxide.

Reaction of 2 with Diethyl Peroxide. To a stirred solution of 1.92 g (0.01 mol) of **2** in 3 g of methylene chloride at 10° was added 0.90 g (0.01 mol) of diethyl peroxide in 1 g of methylene chloride. The reaction mixture was allowed to come to room temperature and it was stored in a desiccator in a refrigerator. The course of the reaction was monitored by ^{31}P nmr spectroscopy. After 24 hr the absorption at −25 was barely detectable while that at −1.5 was essentially unchanged. The reaction mixture was allowed to warm to room temperature and within 24 hr the −1.5 absorption disappeared and the major absorption was found at +36. There was a small absorption at +2.

Reaction of 4 and 5 with Diethyl Peroxide. To a nitrogen-filled 8-ml vial was added 0.005 mol of the phosphine. Enough solvent (methylene chloride or chlorobenzene), dried over molecular sieves, was then added to give a 25% by weight solution of the phosphine. The solution was cooled to −10° in an ice–acetone bath and 0.451 g (0.005 mol) of diethyl peroxide was added. The solutions were stored in a refrigerator and the course of the reactions was monitored by nmr. Benzoic acid was added to the reaction mixtures and it was shown by glpc that ethyl benzoate was formed. Injection of the reaction mixtures into the gas chromatograph showed only the appropriate phosphine oxide as the materials of long retention time. The ^{1}H and ^{31}P nmr spectral data have been reported in the Results.

Reaction of 7 and 8 with Diethyl Peroxide. The ^{31}P nmr spectrum of the mixture of **7** and **8** showed one major absorption at −3.5 (J_{PCH} = 40 Hz). Quin, *et al.*,[11] report J_{PCH} = 40 Hz for **8**. A minor absorption was found at +17; this is assigned to **7**.

To a stirred solution of 0.825 g (0.0046 mol) of the mixture of phosphines in 2.5 g of methylene chloride was added, at −5°, 0.414 g (0.0046 mol) of diethyl peroxide in 1 g of methylene chloride. There was no detectable exotherm. The reaction mixture was allowed to warm to room temperature slowly. After 24 hr the ^{31}P nmr spectrum showed one major absorption at −156 and two minor absorptions at −59 and −4. These are assigned to diethyl phenylphosphonite, phosphine oxide, and starting phosphine. After 1 week the spectrum was essentially unchanged except for a very small absorption at +56 which corresponds to tetraethoxyphenylphosphorane.[5] Addition of authentic diethyl phenylphosphonite augmented the absorption at −156.

Glpc of the reaction mixture on a 6-ft silicone gum rubber column at 70° showed the presence of diethyl phenylphosphonite both by retention time and peak augmentation with authentic phosphonite.

In a separate but identical reaction the ^{1}H nmr spectrum was monitored and the production of isoprene was observed. Glpc analysis of the mixture on a 50-ft silicone gum rubber column at ambient temperature verified the presence of isoprene by retention time and peak augmentation with isoprene.

Competitive Reactions of Phosphines with Diethyl Peroxide and Ethyl Iodide. Each pair of phosphines, *ca.* 1×10^{-3} *M*, was weighed into an nmr tube which was flushed with argon. The nmr tube was thermostated at 22° and to it was added 0.5 ml of diethyl peroxide in cyclopentane. The nmr tube was sealed with a plastic cap and tape and the reaction was allowed to proceed at 22°. Similar procedures were followed in the other solvents. The ratio of products to reactants was determined by peak area measurements (planimeter) of the ^{31}P nmr absorptions in the diethyl peroxide cyclopentane series and peak heights in the other.

The reactions of ethyl iodide were carried out as described for diethyl peroxide except that ethyl iodide in acetonitrile was added to the mixture of the two phosphines.

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