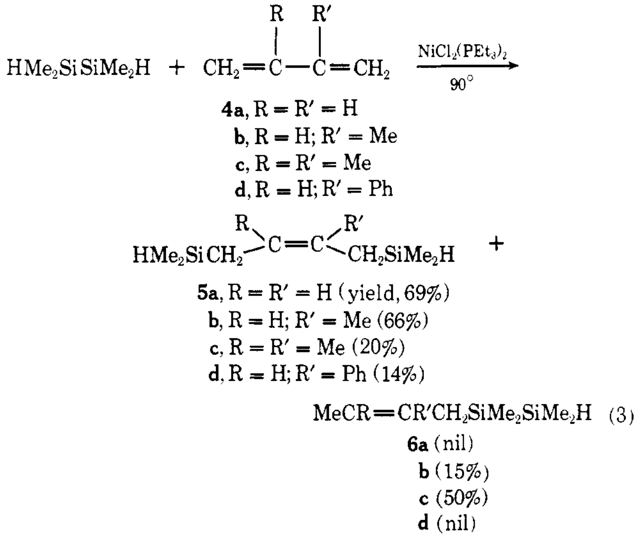
sible isomers, **3d** (R = Me; R′ = Bu), **3d** (R = Bu; R′ = Me), and **3d** (R, R′ = alternate Me and Bu), was obtained in a ratio of 32:12:56. It should be noted that without added acetylene, the disproportionation of *sym*-tetramethyldisilane proceeded with accumulation of the trisilane (*cf.* eq 1). Furthermore, when dimethyl acetylenedicarboxylate was employed as the acetylene compound, we found that none of the product arising from incorporation of the dimethylsilylene moiety into the acetylene was formed. Further, the redistribution of the disilane did not occur. Methyl melitate was a sole product. The data suggest that dialkyl- and diarylacetylenes react with "dimethylsilylene" under mild conditions in the presence of a nickel catalyst. In contrast, dimethyl acetylenedicarboxylate does not react in a similar manner. We believe that the latter fact results from such strong coordination of the dimethyl acetylenedicarboxylate by the nickel complex catalyst that oxidative addition of the disilane is blocked. Under these conditions "dimethylsilylene" would not be formed.

The reaction of *sym*-tetramethyldisilane with a variety of butadienes has also been studied in the presence of the same nickel catalyst. The reaction with butadiene has been found to give a major product which is doubly silylated at the 1,4 positions of the diene. In some cases, considerable amounts of the hydrosilylation product are also formed. The 1,4-double silylation process tends to be counteracted by the hydrosilylation process (eq 3).



$$HMe_2SiSiMe_2H + CH_2{=}C(R){-}C(R'){=}CH_2 \xrightarrow[90^\circ]{NiCl_2(PEt_3)_2}$$

4a, R = R′ = H
b, R = H; R′ = Me
c, R = R′ = Me
d, R = H; R′ = Ph

$$HMe_2SiCH_2(R)C{=}C(R')CH_2SiMe_2H \; +$$

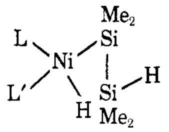
5a, R = R′ = H (yield, 69%)
b, R = H; R′ = Me (66%)
c, R = R′ = Me (20%)
d, R = H; R′ = Ph (14%)

$$MeCR{=}CR'CH_2SiMe_2SiMe_2H \quad (3)$$

6a (nil)
b (15%)
c (50%)
d (nil)

The observed reactions involving *sym*-tetramethyldisilane, an olefinic or acetylenic compound, and a phosphine–nickel(II) complex fall into four types: (i) disproportionation proceeding in the presence or absence of an olefinic compound to form several homologous members of polysilanes of the formula $H(Me_2Si)_nH$; (ii) simple addition of the silicon–hydrogen bond across an olefinic bond (hydrosilylation);[10] (iii) generation of "dimethylsilylene" species, which are effectively trapped by an added acetylenic compound; and (iv) cleavage of the silicon–silicon bond followed by 1,4 addition of the resultant silyl groups (double silylation). These four processes may well be interrelated to each other from the mechanistic point of view.

The novel feature about these reactions can be visualized as proceeding *via* the following steps. First, there occurs oxidative addition of *sym*-tetramethyldisilane to the nickel catalyst. (It is assumed that the metal atom is in a low oxidation state as a result of initial reduction by the silicon hydride.) The following highly active intermediate **7** is then postulated



7, L,L′ = phosphine or unsaturated hydrocarbon ligands

Subsequently, either elimination of dimethylsilane to leave the "dimethylsilylene" on nickel or cleavage of the silicon–silicon bond to form a bis(dimethylsilyl)-nickel complex is assumed. An alternative pathway for the formation of 1,4-bis(dimethylsilyl)-2-butenes is also conceivable. This involves initial addition of "dimethylsilylene" to butadiene to give 1-dimethylsilylbutadiene[11] which then undergoes hydrosilylation with dimethylsilane produced as a result of the α elimination of *sym*-tetramethyldisilane.

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[10] There has been preliminary evidence that the metal complex catalysts cause the hydrogen–silicon bond to scramble as well as labilize the silicon–silicon bond of *sym*-tetramethyldisilane. The observed *hydrodisilanylation* of butadiene without cleavage of the silicon–silicon bond should be noted in this regard.

[11] Skell and Goldstein[12] have reported that dimethylsilylene adds to ethylene to give dimethylvinylsilane by rearrangement.

[12] P. S. Skell and E. J. Goldstein, *J. Amer. Chem. Soc.*, **86**, 1442 (1964).

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Fragmentation of Phosphoranes

Sir:

Several methods are now available for the synthesis of pentacovalent phosphorus compounds[1–6] and of these the routes *via* condensation of trivalent phosphorus compounds with (a) α-dicarbonyl compounds and (b) diethyl peroxide[2] are the most well established. For the second reaction a considerable body of evidence is accumulating to indicate that the reaction is a concerted biphilic addition of the peroxide to trivalent phosphorus *via* a transition state represented by **1**.[7,8] The geometry of the transition state is, however, unknown.

The reaction of 3-methyl-1-phenyl-3-phospholene (**2**) with diethyl peroxide takes an unusual course in that the phosphorane (**3**) formed initially fragments

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[1] F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

[2] (a) D. B. Denney and D. H. Jones, *J. Amer. Chem. Soc.*, **91**, 5821 (1969); (b) D. B. Denney, D. Z. Denney, B. C. Chang, and K. L. Marsi, *ibid.*, **91**, 5243 (1969).

[3] B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell, and D. W. White, *ibid.*, **93**, 4004 (1971).

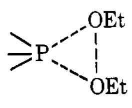
[4] M. Sanchez, L. Beslier, J. Roussel, and R. Wolf, *Bull. Soc. Chim. Fr.*, 3053 (1969).

[5] J. Wilff and R. Huisgen, *Chem. Ber.*, **102**, 1841 (1969).

[6] W. G. Bentrude, W. D. Johnson, and W. A. Khan, *J. Amer. Chem. Soc.*, **94**, 3058 (1972).

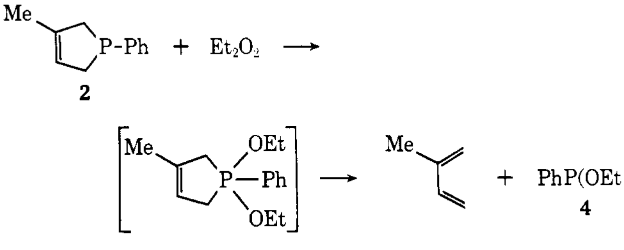
[7] D. B. Denney, D. Z. Denney, C. D. Hall, and K. L. Marsi, *ibid.*, **94**, 245 (1972).

[8] D. B. Denney, private communication.



1

spontaneously at room temperature to give isoprene and diethyl phenylphosphonite[7] (**4**). We have examined

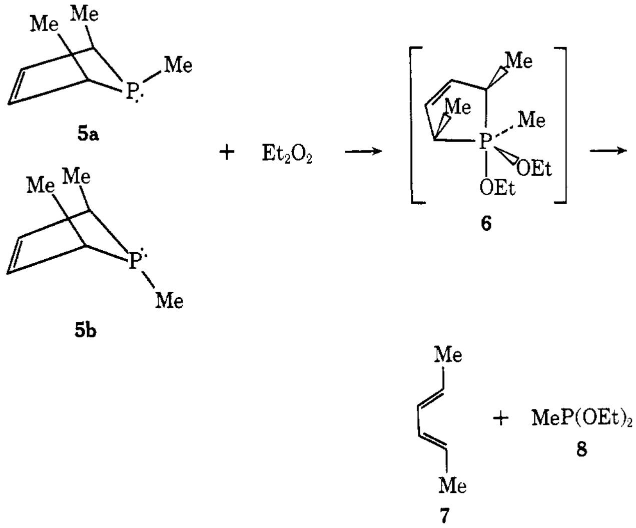


2

3

4

the stereochemistry of this novel fragmentation process by reacting a mixture of *cis,cis-* and *cis,trans*-1,2,5-trimethyl-3-phospholene[9] (**5a,b**) with diethyl peroxide in cyclopentane. The result was formation of *trans,trans*-hexa-2,4-diene (**7**) in quantitative yield together with diethyl methylphosphonite (**8**). The reaction was



5a

5b

6

7

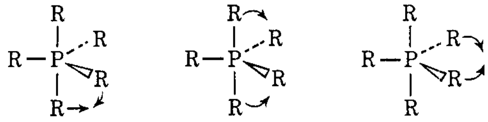
8

99% stereospecific as determined by glc on a 10-ft ODP on Chromosorb G column[10] and it must be concluded that the fragmentation is a concerted, disrotatory process as predicted for a $4n + 2$ electron system;[11] analogous stereochemistry is observed in the diene–sulfur dioxide reaction.[12,13] The reaction is complicated by the subsequent (somewhat faster) reaction of **8** with diethyl peroxide to give methyltetraethoxyphosphorane, $MeP(OEt)_4$ (**9**) ($\delta^{31}P$ +44.7 ppm), but a careful search of the ^{31}P nmr spectrum revealed no evidence for the intermediate phosphorane **6** and the fragmentation is therefore rapid relative to the initial bimolecular reaction to **6**. A kinetic study is in progress to confirm this point but it should be noted that **5a** and **5b** react at very similar rates and the overall disappearance of **5** matches the rate of appearance of **8** and **9**.

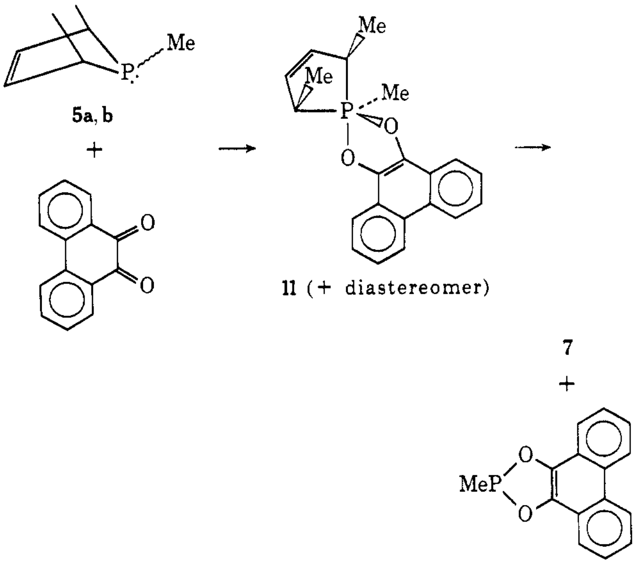
Very recently, Hoffmann considered the hypothetical fragmentation

$$R_5P \longrightarrow R_3P + R_2$$

from the standpoint of orbital symmetry correlations and came to the startling conclusion that from a trigonal-bipyramid structure (D_{3h}) the allowed processes were e–e (**10a**) or a–a (**10b**) departure of R_2, whereas the least motion pathway, e–a (**10c**), was symmetry forbidden.[14] We have since shown that reaction of **5a,b** with phenanthraquinone in $CDCl_3$ at 25° gives a relatively stable phosphorane **11**, $\delta^{31}P(H_3PO_4)$ −27 ppm.[15] This phosphorane also fragments stereospecifically to *trans,trans*-hexa-2,4-diene and the cyclic phosphonite **12**, but the half-life at 44° is *ca.* 2.0 hr giving $\Delta G^{\ddagger} \approx 25$ kcal mol^{-1}. The phosphorane **11** would undoubtedly prefer the geometry shown in order to fulfill the strain and polarity rules[16] but if e–a departure is allowed there is no reason in principle why the free energy of activation for the fragmentation of **11** should be much greater than that for **6** unless one assumes that the factor responsible for the difference in $\Delta G^{\ddagger}$ values is an inherent high stability of spirophosphoranes such as **11** in comparison with monocyclic phosphoranes.



10c, e-a 10b, a-a 10a, e-e



5a, b

11 (+ diastereomer)

7

12, $\delta^{31}P$ −212

There is, however, an alternative explanation. If the phospholene ring can only fragment from the phos-

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[9] The diastereomeric mixture of 3-phospholenes (ratio **5a**:**5b**, 4:1) was prepared by reduction of the diastereomeric oxides using phenylsilane (K. L. Marsi, F. B. Burns, and R. T. Clark, *J. Org. Chem.*, 37, 238 (1972)), the mixture of oxides being obtained by the method of Green, *et al.*: A. Bond, M. Green, and S. C. Pearson, *J. Chem. Soc. B*, 929 (1968).

[10] B. Smith, R. Ohlsen, and G. Larson, *Acta Chem. Scand.*, **17**, 436 (1963).

[11] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

[12] W. L. Mock, *J. Amer. Chem. Soc.*, **88**, 2857 (1966).

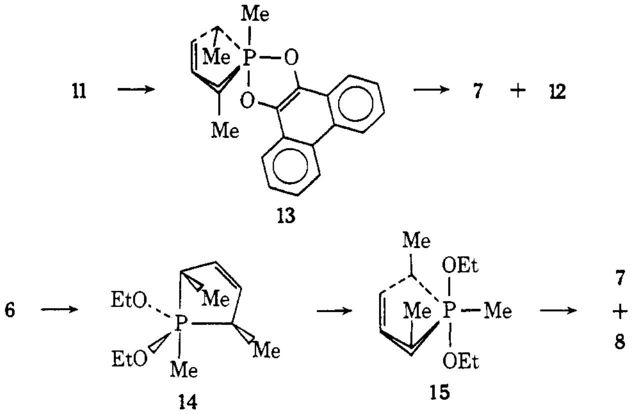
[13] S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2859 (1966).

[14] R. Hoffmann, J. M. Howell, and E. L. Muetterties, *ibid.*, **94**, 3047 (1972).

[15] Although this value is abnormally low for a phosphorane, the possibility of a dipolar structure is negated by the observation of an almost identical chemical shift (−26.5 ppm) in cyclopentane; see ref 1. For a bicyclic phosphorane with an unusually low ^{31}P chemical shift see N. J. De'Ath and D. B. Denney, *J. Chem. Soc., Chem. Commun.*, 395 (1972).

[16] Principles are outlined in the following articles: K. Mislow, *Accounts Chem. Res.*, **3**, 321 (1970); E. L. Muetterties, *ibid.*, **3**, 266 (1970); F. H. Westheimer, *ibid.*, **1**, 70 (1968); ref 1.

phorane by e–e departure[17] the pseudorotation **11** → **13** violates the strain rule (17–22 kcal mol^{-1} energy loss),[18] whereas the energy loss in placing the phospholene ring of **6** diequatorial by pseudorotation **6** → **15** *via* **14** is compensated for by placing two electro-



negative ethoxy groups in apical positions (energy gain, 10–17 kcal mol^{-1}).[18] This argument is supported by the free energy of activation for fragmentation of **11** which is very close to the energy barrier established by Gorenstein for switching of a five-membered ring from an e–a to an e–e conformation.[18a] Hence, a large part of $\Delta G^{\neq}$ for fragmentation probably arises from this energetically unfavorable pseudorotation.

Thus the evidence suggests that Hoffmann's orbital-symmetry predictions are correct. Indeed, if one accepts that attack of peroxide on trigonal phosphorus is a biphilic process, the peroxide molecule may well enter e–e (**5a,b** → **14**) which may pseudorotate rapidly to **15** and hence fragment to **7** and **8**.

Acknowledgment. Thanks are due to California State University—Long Beach for an equipment grant and to California Institute of Technology for the use of nmr facilities. The advice of Dr. D. B. Denney (Rutgers University) is also gratefully acknowledged.

(17) a–a disposition of the five-membered ring is impossibly strained.

(18) (a) D. Gorenstein, *J. Amer. Chem. Soc.*, **92**, 644 (1970); (b) D. Houlla, R. Wolf, D. Gagnoire, and J. B. Robert, *Chem. Commun.*, 443 (1969).

(19) On leave from King's College, London.

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Reductive Silylation of Molecular Nitrogen *via* Fixation to Tris(trialkylsilyl)amine

Sir:

In the course of studies concerned with the reductive silylation of benzene derivatives employing a Nichrome-wire high-speed stirrer, the author found remarkably that the molecular nitrogen used as an inert atmosphere was taken up at room temperature and reductively silylated to trissilylamine.

$$6(CH_3)_3SiCl + 6Li + N_2 \xrightarrow[\text{THF}]{\text{transition metal}} 2N[Si(CH_3)_3]_3 + 6LiCl$$

In order to obtain more information on the nature of this direct transformation of molecular nitrogen into trissilylamine, a number of reactions were carried out in the presence of a variety of transition metal compounds, mainly their chlorides (Table I).

Table I. Effect of Various Catalysts on Reductive Silylation of Nitrogen

Catalyst	Mol ratio of silylamine to transition metal	Catalyst	Mol ratio of silylamine to transition metal
$TiCl_4$	0.8	$NiCl_2$	0.2
Cp_2TiCl_2	0.8	CuCl	0.0
VCl_3	0.9	$CuCl_2$	0.0
$CrCl_3$	5.4	$MoCl_5$	1.0
$MnCl_2$	1.2	WCl_6	0.2
$FeCl_3$	2.3	$PdCl_2$	0.0
$FeCl_2 \cdot 4H_2O$	0.6	$RuCl_3 \cdot H_2O$	0.0
$CoCl_2$	1.2	None	0.0

One of the reactions which gave the highest yield of silylamine, for example, was that under the following conditions: a mixture of 1.6 g (0.01 mol) of chromium chloride, 54.0 g (0.5 mol) of trimethylchlorosilane, and 3.5 g (0.5 g-atom) of cut lithium wire in 150 ml of dry THF was stirred at room temperature for 30 hr under 1 atm of dry nitrogen. At an initial stage of this reaction, the mixture darkened with evolution of heat, followed by fairly rapid absorption of nitrogen. The absorption of nitrogen slowed down after several hours. After separation of unreacted lithium metal, distillation of the homogeneous black filtrate gave a fraction boiling at 50–100° (26 mm). Further purification by fractional distillation gave pure tris(trimethylsilyl)amine: 10.0 g; bp 97–98° (26 mm); mp 69–71°; pmr (CCl_4), singlet at 0.19 ppm ($Si-CH_3$, no other protons present); ir, strong absorption at 915 cm^{-1} (Si–N stretching); reported[1] for $[(CH_3)_3Si]_3N$, bp 76° (12 mm), mp 70–71°. Tris(dimethylethylsilyl)amine was similarly prepared in lower yield, because of increased consumption of dimethylethylchlorosilane by coupling on lithium metal to give disilane.[2]

Whenever nitrogen was absorbed, regardless of its quantities, the system darkened and trissilylamine appeared. Not only the reaction mixtures, but also the black residues left after distillation were soluble even in benzene and *n*-hexane to give a homogeneous solution.

Although the yields were small, the silylamine was also obtained when sodium and potassium metal were used as a reducing agent with chromium(III) acetylacetonate.

The formation of nitride as a completely reduced species of fixed nitrogen, prior to ammonia by hydrolysis, has been postulated by some investigators.[3,4] This species, however, so far has not been fully characterized. The fact that insufficient reduction of molecular nitrogen on transition metals results in the formation of hydrazine by protonation[5] seems to support

(1) J. Gaubeau and J. Jimenz-Barbera, *Z. Anorg. Allgem. Chem.*, **303**, 217 (1960).

(2) H. Gilman, K. Shiina, D. Aoki, B. J. Gaj, D. Wittenberg, and T. Brennan, *J. Organometal. Chem.*, **13**, 323 (1968).

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(4) E. E. van Tamelen, *Accounts Chem. Res.*, **3**, 361 (1970), and references cited therein.

(5) E. E. van Tamelen, R. B. Fechter, and S. W. Schneller, *J. Amer. Chem. Soc.*, **91**, 7196 (1969).