Tetrahedron Letters,Vol.25,No.33,pp 3519-3520,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

THE REACTION OF PHOSPHINYL RADICALS WITH 1,3-DIENES

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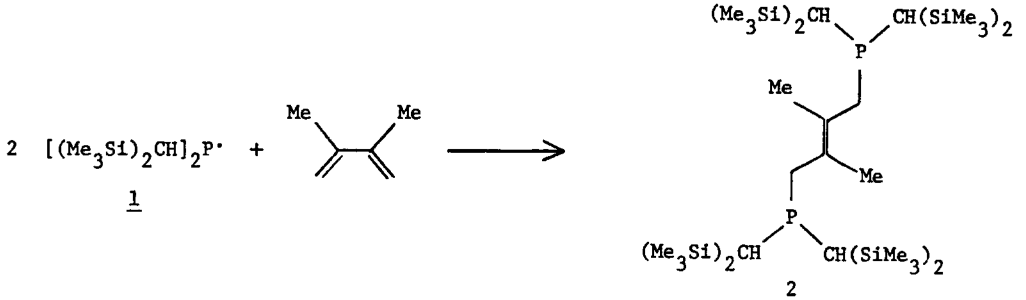
The stabilized radical, $[(Me_3Si)_2CH]_2P\cdot$, reacts with 1,3-dienes to afford 1,4-diphosphino-2-butenes.

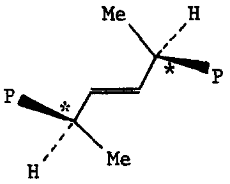
Phosphinyl radicals ($R_2P\cdot$) have long been implicated as intermediates in the reactions of diphosphines with C=C and C≡C bonds. Thus pioneering work by Burg[1], Chatt[2] and co-workers in the 1960's established that alkylated diphosphines will add to alkenes and alkynes. Similar reactions have been reported subsequently for other diphosphines[3] and secondary phosphines.[4] In some instances, kinetic studies implied the intermediacy of $R_2P\cdot$ species. Kinetically-stabilized radicals such as $[(Me_3Si)_2CH]_2P\cdot$ (1) have now become available[5]; however, relatively little is known about their reactivities. We have now found that *e.g.* 1 reacts readily with carbon-carbon double and triple bonds. Our work thus supports the possible intermediacy radicals in these reactions.

Solutions of 1 in *n*-hexane at room temperature exhibit an intense blood-red color typical of a radical species. Addition of an equimolar quantity of 2,3-dimethyl-1,3-butadiene causes fading of the color over a 45 minute period. Workup of the solution affords white crystals of 2[†], mp 198-202°C. A $^{31}P\{^1H\}$ NMR spectrum of 2 comprises a singlet at -3.3 ppm. This, together with ^1H and ^{13}C NMR data, suggest a 1,4-diphosphino-2-butene structure for 2.

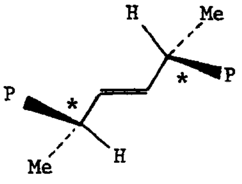


The *trans* geometry about the C=C double bond is expected on the basis of steric arguments. This was tentatively confirmed by an X-ray structure of 2. Suitable crystals of 2 were obtained from CH_2Cl_2 and intensity data were collected on an Enraf-Nonius CAD-4 diffractometer. However, subsequent refinement revealed a severe disorder problem associated with one $P[CH(SiMe_3)_2]_2$ moiety. While it was not possible to solve the structure completely, a *trans* geometry around the central double bond was clearly apparent. Full details will be presented elsewhere.

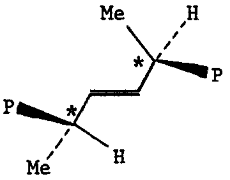
The phosphinyl radical, 1, also reacts with an equimolar quantity of *trans*-2-*trans*-4-hexadiene in *n*-hexane, albeit more slowly, taking 24 hours to reach completion. The $^{31}P\{^1H\}$NMR spectrum of the product, 3[†], showed two resonances at 15.99 (3a) and 15.81 (3b) ppm. It is proposed that 3 adopts a similar structure to that of 2. However, in 3, unlike 2, a chiral center is generated at the 1 and 4 carbon atoms on addition of the phosphinyl groups. Four possible isomers result from the generation of these two chiral centers resulting in two sets of two enantiomers. Since each pair is diastereomeric, the occurence of two ^{31}P NMR resonances is thus rationalized.



S,S

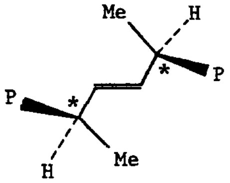


R,R



R,S

P = $[(Me_3Si)_2CH]_2P$



S,R

Acknowledgment. We thank the National Science Foundation and the Robert A. Welch Foundation for generous financial support.

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Footnotes

[†] Satisfactory analytical data were obtained for 2 and 3.

(Received in USA 30 January 1984)