Remarkable Differences in the Reactivities of the (*E*)- and (*Z*)-Isomers of a Phospha-alkene

Andrew R. Barron, Alan H. Cowley,* and Stephen W. Hall

Department of Chemistry, The University of Texas at Austin, Austin, Texas, 78712 U.S.A.

The (*E*)- and (*Z*)-isomers of the phospha-alkene, $\mathrm{Bu^t(Me_3SiO)C{=}PSiMe_3}$, show markedly different reactivities towards heat and molecular oxygen.

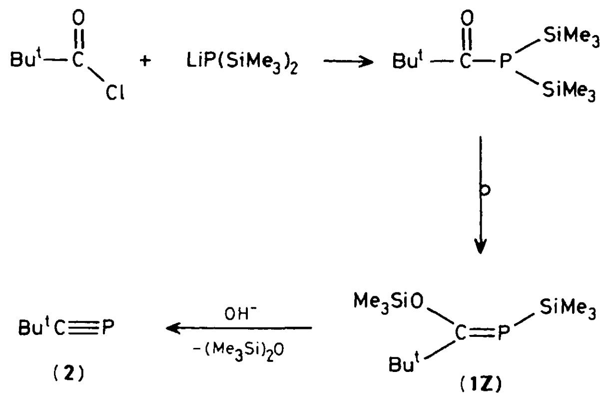
Pioneering work by Becker *et al.*[1] established that the sequence of reactions in Scheme 1 leads to $\mathrm{Bu^tC{\equiv}P}$, a stable phospha-alkyne which has proved to be of importance both as a reagent[2] and as a ligand.[3] Only the (*Z*)-isomer of the phospha-alkene, $\mathrm{Bu^t(Me_3SiO)C{=}PSiMe_3}$, was formed when the reaction of $\mathrm{Bu^tC(O)Cl}$ with $\mathrm{LiP(SiMe_3)_2}$ took place at 20 °C. We have now found that (i) conducting this reaction at −78 °C results in exclusive formation of the phospha-alkene isomer, (**1*E***), (ii) the reactivities of (**1*E***) and (**1Z**) are markedly different, and (iii) (**1*E***) is converted rapidly into (**2**) by a novel catalytic oxygenation.

Treatment of $\mathrm{Bu^tC(O)Cl}$ with $\mathrm{LiP(SiMe_3)_2}$ in cyclopentane solution at −78 °C rather than 20 °C resulted in the formation of (**1*E***). As expected, the n.m.r. data for the two isomers are rather similar;† however, (**1*E***) and (**1Z**) can be differentiated by the fact that the $^2J_{\mathrm{PC}}$ and $^3J_{\mathrm{PC}}$ coupling constants are significantly larger for the latter owing to the *cis* relationship of the $\mathrm{Bu^t}$ group and the phosphorus lone pair.[4] We have

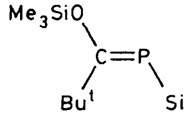
---

† N.m.r. spectra recorded at ambient temperature relative to 85% $\mathrm{H_3PO_4}$ (^{31}P) or $\mathrm{SiMe_4}$ (^{13}C). Compound (**1Z**) $^{31}\mathrm{P}\{^1\mathrm{H}\}$ n.m.r. (32.2 MHz) δ + 120 p.p.m. (s); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ n.m.r. (75.4 MHz) δ 0.9 (d, $^2J_{\mathrm{PC}}$ 8.3 Hz, PSiC), 2.0 (s, OSiC), 30.5 (d, $^3J_{\mathrm{PC}}$ 9.8 Hz, PCC*C*), 45.0 (d, $^2J_{\mathrm{PC}}$ 24.9 Hz, PC*C*), 227 (d, $^1J_{\mathrm{PC}}$ 80.5 Hz, PC).

Compound (**1*E***) $^{31}\mathrm{P}\{^1\mathrm{H}\}$ n.m.r. (32.2 MHz) δ + 124 p.p.m. (s); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ n.m.r. (75.4 MHz) δ 0.9 (d, $^2J_{\mathrm{PC}}$ 8.1 Hz, PSiC), 2.0 (s, OSiC), 30.7 (d, $^3J_{\mathrm{PC}}$ 2.0 Hz, PCC*C*), 45.2 (d, $^2J_{\mathrm{PC}}$ 12.2 Hz, PC*C*), 229 (d, $^1J_{\mathrm{PC}}$ 80.6 Hz, PC).



Scheme 1



(1*E*)

found no evidence for the interconversion of (**1***E*) and (**1***Z*) either photochemically or thermally.

The literature method for converting (**1***Z*) into (**2**) involves treatment with NaOH in diethylene glycol dimethyl ether.[1] We have found that higher yields of (**2**) can be realised by heating (**1***Z*) at 140 °C in the absence of a solvent. Interestingly, no (**2**) was detected when (**1***E*) was heated under the same conditions. Monitoring of these reactions by 70 eV electron impact mass spectrometry revealed that whilst (**1***Z*) decomposed by $(Me_3Si)_2O$ loss, (**1***E*) eliminated Bu^tSiMe_3 and only traces of $(Me_3Si)_2O$ were detectable.

Of particular interest is the fact that in the presence of small quantities of molecular oxygen, cyclopentane solutions of (**1***E*) are converted into (**2**) in quantitative yields, thus representing a significantly improved synthesis of this phospha-alkyne. By contrast, oxygenation of (**1***Z*) does not produce (**2**), but results only in decomposition. We do not have any evidence on the mechanism of the reaction; however, it is possible that it proceeds *via* oxygenation at the phosphorus atom of (**1***E*), a process previously observed by Bickelhaupt *et al.*,[5] followed by Me_3Si migration‡ and elimination of $(Me_3Si)_2O$. In independent experiments we have demonstrated that (**2**) is unreactive towards O_2.

Finally, we note that both (**1***E*) and (**1***Z*) are converted into (**2**) in high yield by treatment with a stoicheiometric quantity of $Fe_2(CO)_9$. Since both the (*E*)- and (*Z*)-isomers react with $Fe_2(CO)_9$ in an identical manner, we propose that the reaction proceeds *via* an η^2-phospha-alkene $Fe(CO)_4$ complex which decomposes to (**2**) and oligomeric iron siloxy–silyl compounds.

We are grateful to the U.S. Army Research Office and the Robert A. Welch Foundation for financial support.

Received, 19th January 1987; Com. 065

References

1 G. Becker, G. Gresser, and U. Uhl, *Z. Naturforsch., Teil B*, 1981, **36**, 16; G. Becker, *Z. Anorg. Allg. Chem.*, 1977, **430**, 66; 1981, **480**, 21.

2 R. Appel, F. Knoll, and I. Ruppert, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 731; G. Becker, W. Becker, and O. Mundt, *Phosphorus Sulfur*, 1983, **14**, 267; E. A. Ishmaeva and I. I. Patsanovskii, *Russ. Chem. Rev. (Engl. Transl.)*, 1985, **54**, 243.

3 P. B. Hitchcock, M. J. Maah, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1986, 737, and references therein; O. J. Scherer, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 924.

4 G. Becker, O. Mundt, and G. Uhl, *Z. Anorg. Allg. Chem.*, 1984, **517**, 89; M. Yoshifuji, K. Toyota, and N. Inamoto, *Tetrahedron Lett.*, 1983, **24**, 1653.

5 T. A. van der Knaap, T. C. Klebach, R. Lourens, M. Vos, and F. Bickelhaupt, *J. Am. Chem. Soc.*, 1983, **105**, 4026.

---

‡ The oxidation of P–$SiMe_3$ compounds results in P–O–$SiMe_3$ moieties, *e.g.* the reaction of O_2 with Ph_2SiMe_3 produces $PH_2P(O)$-$SiMe_3$.