Tetrahedron Letters Vol. 21, pp 4791 - 4794
Printed in Great Britain
0040-4039/80/1208-4791$02.00/0

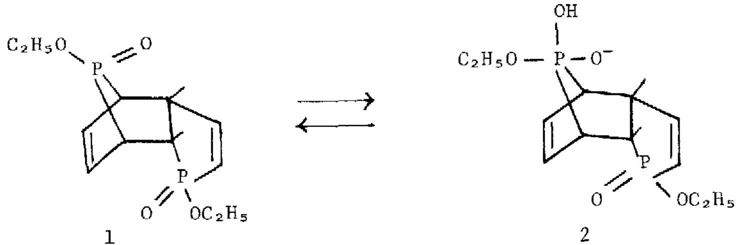
SYN TO ANTI ISOMERIZATION AND DEGRADATION OF PHOSPHINES OF THE 7-PHOSPHANORBORNENE SYSTEM BY ACTION OF METHANOL

Keith A. Mesch and Louis D. Quin*

Cross Chemical Laboratory, Duke University, Durham, North Carolina, 27706

Abstract. *Syn*-Substituted phosphines of the 7-phosphanorbornene system form unstable phosphorane adducts with methanol that either fragment by retro-McCormack cycloaddition or undergo polytopal rearrangement and loss of methanol to give the first examples of *anti* phosphines.

When angle strain is severe about phosphorus in P(III) or P(IV) structures, the formation of phosphorane intermediates or products can occur with exceptional ease. A well-known example[1] of the latter is the remarkably fast hydrolysis rate of the phosphinate group when incorporated in the 7-position of the norbornene skeleton as in 1. Here the rate for basic hydrolysis is about 10^5 that of unstrained, noncyclic phosphinates due to the greater compatibility of the constrained C-P-C angle (87°[2]) with the requirements of the apical-equatorial position (90°) of trigonal bipyramidal intermediate 2 than of the tetrahedral structure 1.



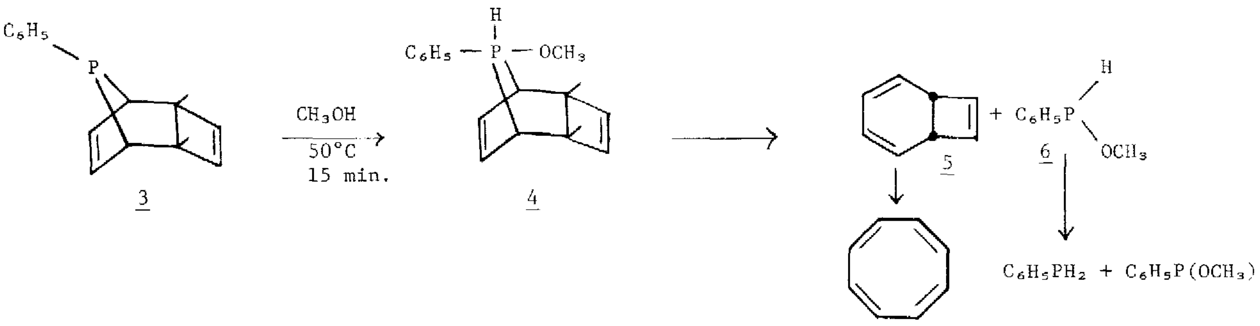
1 2

Similarly, phosphines of the strained phosphetane system form dialkoxyphosphoranes on reaction with $(RO)_2$ at a rate faster than that of acyclic phosphines.[3]

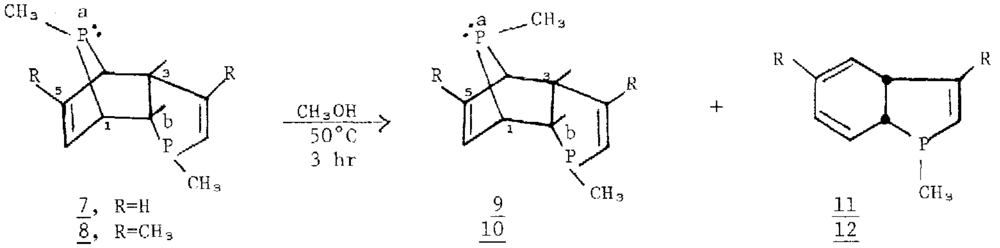
Following our recent synthesis of the first tertiary phosphines of the 7-phosphanorbornene series[4], we have encountered two chemical changes with these strained substances that require an explanation based on the unprecedented intermediacy of a P(V) adduct with methanol or water. While alcohols are known to form adducts with certain phosphite derivatives[5], no adduct of this type has ever been reported for a phosphine.

Warming the 7-phosphanorbornene 5[4] with methanol results in its complete destruction within 15 minutes. The products are cyclooctatetraene, phenylphosphine and dimethyl phenylphosphonite. Each of these are secondary products whose origins are explained in Scheme 1. The key steps are the formation of P(V) adduct 4 and its subsequent degradation by a reverse McCormack cycloaddition to a diene (5) and a phosphinite (6). Another example[3,6] of a reverse McCormack reaction is provided by the P(V) adduct of a 3-phospholene with a dialkyl peroxide; degradation is rapid to form a diene and a phosphonite. Just as for the initial products from adduct 4, the forward McCormack reaction is not known to occur with the released phosphonite. The ejected monoalkylphosphinite 6 from the reverse McCormack reaction of 4 then undergoes disproportionation to the observed products (detected by ^{31}P NMR at δ -123 for the phosphine and δ +160 for the phosphonite; upfield and downfield, respectively, from 85% H_3PO_4), while the diene undergoes rearrangement[7] to cyclooctatetraene. No spectral evidence for the intermediacy of the proposed P(V) form has yet been obtained.

Scheme 1

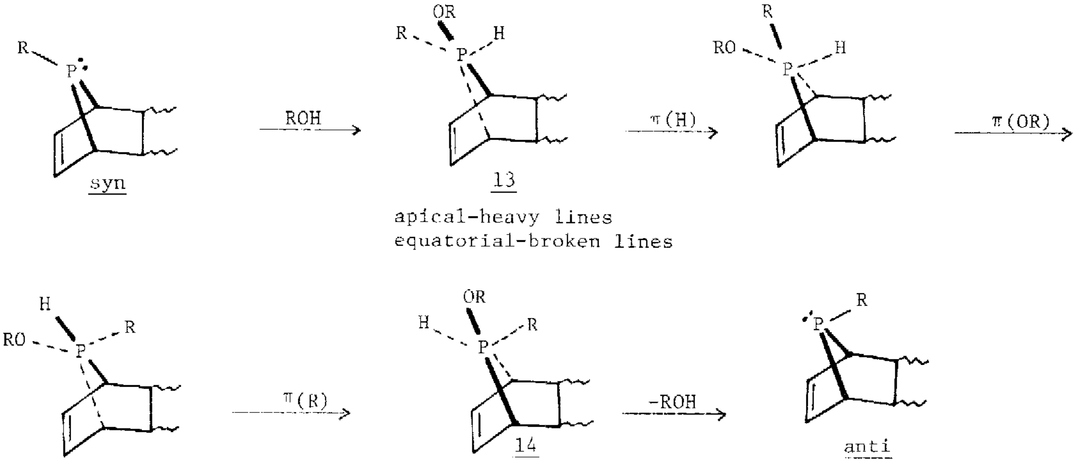


7-Phosphanorbornene derivative 7[4] was slower in its degradation with methanol, and after 3 hr. at 50° only 20% had decomposed by the reverse McCormack pathway (as determined by the concentration of dihydrophosphindole derivative 11, δ ^{31}P +11.7). However, the surprising observation was made that 64% of the phosphine had undergone inversion of configuration at the bridging phosphorus to produce the anti isomer (9). The mixture also contained some unrearranged 7 (16%). With phosphine 8[4], the inversion was nearly complete (96% of 10, 4% of 12), allowing the isolation of the anti isomer in pure form by distillation (78% yield). The reaction can therefore be viewed as having preparative value.



A solution of water in dioxane behaved in the same manner: with the P-phenyl counterpart[4] of 8, 90% inversion and 10% reverse-McCormack reaction occurred after 16 hr. at 50°. That the isomerization at P depends on a direct reaction with the hydroxylic species and is not a simple pyramidal inversion with an unusually low $\Delta G^{\ddagger}$ is suggested from the failure of the syn-phosphines to isomerize when heated neat or in solvents such as dioxane, benzene, $CDCl_3$[8], or CH_3CN. The isomerization can be explained by the intermediacy of the same P(V) adduct that is involved in the reverse McCormack reaction. This adduct undergoes rearrangement of the trigonal bipyramid to a form that, on loss of methanol, generates the anti structure. The anti isomer was found to be unchanged when subjected to the alcohol treatment.

While no facts are available that reveal the mechanism of the ROH addition, it may constitute an example of concerted attack of a biphilic species on P(III), a type of reaction recently subjected to theoretical scrutiny[9,10]. A two-step process involving initial formation of a P(IV) intermediate seems unlikely, as angle strain would only be increased in forming such a tetrahedral intermediate. The P(V) adduct can be developed with RO-H occupying equatorial-equatorial[9] or apical-equatorial positions[10]; structure 13 shows the result of the latter approach to a *syn*-phosphine, and the polytopal rearrangements of the trigonal bipyramid required to produce an isomeric structure (14) which on loss of RO-H would generate the *anti*-phosphine.



syn

13

14

anti

apical-heavy lines
equatorial-broken lines

Identification of the *anti*-P-methyl isomers was made by converting them to the same methiodides as formed from the *syn* isomers (from 7, m.p. 197-199°; from 8 m.p. 200-201°). The isomeric phosphines had dramatically different ^{31}P NMR spectra; for example, *syn* isomer 7 has the 7-P at δ +96.5, the *endo* P at δ -2.3 with $^3J_{PP}$=24.4 Hz, while the *anti* isomer (9) has 7-P at δ +30.2, *endo* P at δ -7.9 and shows no P-P coupling. Similarly, no P-P coupling was observed for 10 (δ $^{31}P_a$ +27.1, P_b -9.5). That the magnitude of $^3J_{PP}$ in rigid diphosphorus compounds can be controlled by the configuration at a trivalent phosphorus seems to be a new observation[11], although cases are known where three-bond C-P[12] and H-P[13] couplings in phosphines are so controlled. The isomers show certain ^{13}C NMR differences that are perfectly consistent with the configurational differences assigned to the 7-P. Thus, it is a well-established property[14] that the magnitude of $^2J_{PC}$ in phosphines is increased by proximity to the lone pair, and this is clearly visible on comparing data for pertinent carbons in isomer pair 8 and 10 (at C-5: 8, δ 142.4, $^2J_{CP_a}$=4.2 Hz; 10, δ 144.5, $^2J_{CP_a}$ = 20.1. At C-3: 8, δ 59.6, $^2J_{CP_a}$ = 28.1 and $^2J_{CP_b}$ = 3.0; 10, δ 59.4, $^2J_{CP_a}$= 3.8 and $^2J_{CP_b}$= 4.2). That the *endo*-P_b is not involved in the methanol inversion reaction is obvious from the consistency of $^2J_{CP_b}$ at C-1 (8, δ 47.3, $^2J_{CP_b}$ = 24.5; 10, δ 44.2, $^2J_{CP_b}$=22.5)[15]. Furthermore, the CH_3 signal at P_b has the same chemical shift and coupling constant (δ 15.8, $^1J_{PC}$= 19.5) in both 8 and 10, and would surely differ if the steric environment had been changed.

It is not yet clear why the *syn*-isomer undergoes P(V) formation so much more readily than the *anti*, as revealed by the lack of rearrangement of the *anti* isomer under the same conditions. Nor is it known why the ^{31}P NMR shifts differ so drastically for the isomers. These properties make it obvious that the 7-phosphanorbornene system offers unique opportunities for the detection of novel influences in phosphine chemistry that result from molecular geometry deformations, or unusual orbital interactions, or both.

References

1. R. Kluger and F. H. Westheimer, J. Am. Chem. Soc., 91, 4143 (1969).
2. Y.-Y. H. Chiu and W. N. Lipscomb, J. Am. Chem. Soc., 91, 4150 (1969).
3. D. B. Denney, D. Z. Denney, C. D. Hall, and K. L. Marsi, J. Am. Chem. Soc., 94, 245 (1972).
4. L. D. Quin and K. A. Mesch, J. Chem. Soc. Chem. Comm., in press.
5. To illustrate, a P(V) adduct has been observed spectroscopically from the combination of an aminophosphite with an alcohol. L. Lafaille, F. Mathis, and J. Barrans, Compt. Rend. Acad. Sci. Paris, 285C, 575 (1977).
6. G. Scott, P. J. Hammond, C. D. Hall, and J. D. Bramblett, J. Chem. Soc. Perkin II, 882 (1977).
7. R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, Chem. Soc. Spec. Publ., 19, 3 (1964).
8. Isomerization of phospholenes in $CDCl_3$ through a P(V) intermediate formed from a phosgene impurity has been reported: P. J. Hammond and C. D. Hall, Phosphorus and Sulfur, 3, 351 (1977)
9. R. Hoffman, J. M. Howell, and E. L. Muetterties, J. Am. Chem. Soc., 94, 3047 (1972).
10. J. M. Howell, J. Am. Chem. Soc., 99, 7447 (1977).
11. The conformationally mobile cis, trans isomers of some 1,4-diphosphorinanes can show substantial differences in $^3J_{PP}$; this may be a manifestation of the same phenomenon along with effects due to dihedral angle variations. For some examples, see R. B. King and W. F. Masler, J. Am. Chem. Soc., 99, 4001 (1977).
12. S. Sørensen and H. J. Jakobsen, Org. Magn. Resonance, 9, 101 (1977).
13. An example may be found by examination of data reported by T. J. Katz, C. R. Nicholson, and C. A. Reilly, J. Am. Chem. Soc., 88, 3832 (1966).
14. G. A. Gray and S. E. Cremer, J. Chem. Soc. Chem. Comm., 367 (1972); J. J. Breen, S. I. Featherman, L. D. Quin, and R. C. Stocks, J. Chem. Soc. Chem. Comm., 657 (1972).
15. The large size of this coupling is of value in establishing the configuration at the endo-P. The configuration expressed by structures 7 - 10 places the lone pair in quite close proximity to C-1; the lone pair is remote in the opposite configuration and $^2J_{CP}$ should be quite small.

(Received in USA 18 August 1980)