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THERMOLYSIS OF 2-PHOSPHABICYCLO[2.2.2]OCTA-5,7-DIENES: GENERATION AND TRAPPING OF P-METHYL- AND P-PHENYLPHOSPHAETHENE

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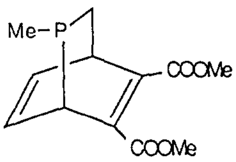
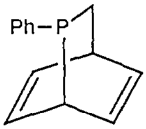
Abstract. P-Methyl- and P-phenylphosphaethene were generated in solution under very mild conditions in virtually quantitative yield by a thermally-induced extrusion of the phosphorus-containing bridge from appropriately substituted 2-phosphabicyclo[2.2.2]octa-5,7-dienes. The phosphaethenes so formed, the simplest yet produced by conventional methods, are trapped readily in [2 + 4] cycloadditions with conjugated dienes.

We have shown earlier[1] that cyclic phosphonates and phosphinates based upon the 2,3-oxaphosphabicyclo[2.2.2]octene system extrude the phosphorus-containing bridge at about 100° to give metaphosphates (ROPO$_2$) and metaphosphonic anhydrides (RPO$_2$), respectively, in high yield. These transient, low-coordination species[2] may be trapped efficiently by P=O addition reactions with alcohols or amines, or by electrophilic substitution on N-methylpyrrole. In principle, this type of fragmentation reaction could be used to prepare numerous other low-coordination species, and we have now devised a technique for the production of phosphaethenes, R-P=CH$_2$. While of considerable current interest,[3] such species are generally prepared with electronegative P-substituents[4] or with very bulky P- and/or C-substituents to endow them with stability.[3,5] The fragmentation process could provide a number of simple, albeit highly reactive, phosphaethenes bearing only a P-substituent, thus allowing a study of their reactivity without the encumbrance of the stabilizing groups. We have found that the 2-phosphabicyclo[2.2.2]octa-5,7-dienes 1 and 2, which we recently reported,[6] do indeed function as precursors of the species MeP=CH$_2$ and PhP=CH$_2$, respectively. This ring system, synthesized in the highly substituted form 3, has been used before[7] in attempts to prepare the oxide and sulfide of PhP=CH$_2$, and it was found that while 3 (X = O) was quite resistant to thermal degradation, the sulfide released the species PhP(S)=CH$_2$ upon heating at 110°.



1



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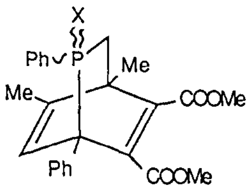


3 (X = O or S)

Phosphines 1 and 2 were found to extrude quite readily the phosphaethenes $MeP=CH_2$ (previously observed[8] in products from the thermolysis at 500° of Me_2PCl) and $PhP=CH_2$ on gentle heating in toluene and other solvents. Phosphine 1 is reasonably stable at room temperature but eliminates the phosphaethene at 40° in about 5 hrs in toluene. At 70°, the elimination is complete in a few minutes. Phosphine 2 is less stable and the elimination of the bridge is very rapid even at 30°. In the absence of a trapping agent, these phosphaethenes undergo intermolecular reactions to give product mixtures with broad ^{31}P NMR signals (e.g., for $MeP=CH_2$ in the range δ -40 to -50), consistent with tertiary phosphines as would arise from head-to-head or head-to-tail reactions.[9] Dimethyl phthalate was isolated from the decomposition of 1 by chromatography and identified by ^{13}C NMR spectroscopy.

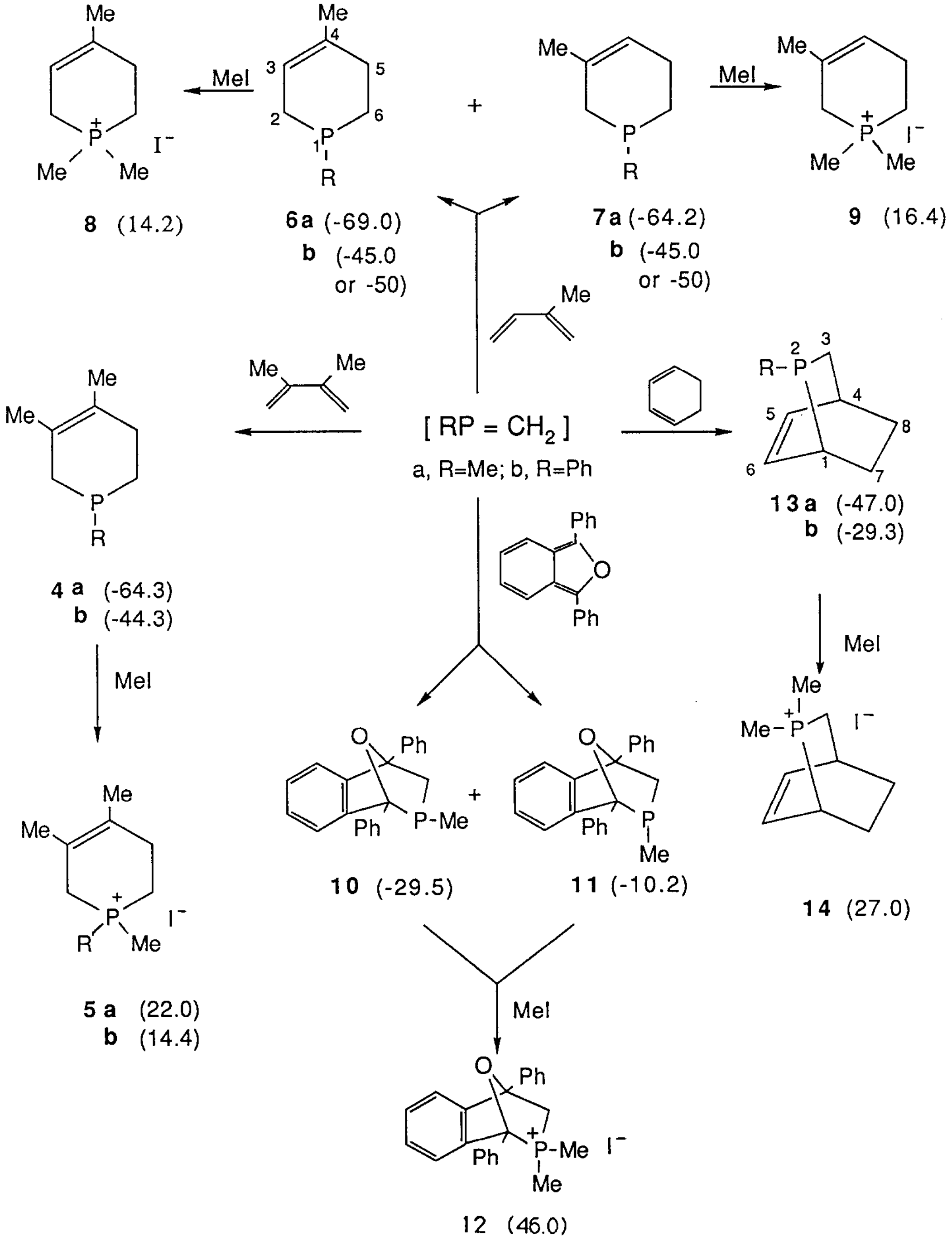
It has been shown[9,10] that 1,3-dienes are particularly efficient trapping agents for phosphaalkenes. Accordingly, $MeP=CH_2$ was generated by heating 1 in toluene at 40-50° in the presence of a variety of dienes (in excess), as shown in Scheme I, to give [2 + 4] cycloaddition products. Analysis of the products by ^{31}P NMR showed all starting phosphine to have been consumed and the only phosphorus signals observed were those for the expected tetrahydrophosphinines. Thus, the process was free of interfering side reactions. The various phosphine products of Scheme I were characterized primarily by ^{31}P NMR, which in some cases (4,6,7) gave spectra similar to those of related compounds in the literature.[11] In the reaction of $MeP=CH_2$ with 1,3-diphenylisobenzofuran, both the exo and endo isomers 10 and 11 were produced, as would be expected by analogy with known[12] reactions of other phosphaalkenes with 2-methylfuran or cyclopentadienes. This was revealed by the presence of two ^{31}P NMR signals (about 1:1), and by the fact that a single quaternary salt (12, not sufficiently stable for reliable analysis) was formed from the isomers on reaction with methyl iodide. Cycloaddition also occurred with furan itself to give isomers with ^{31}P NMR signals at -62.5 and -49.0 in the ratio 4:1, but again neither these nor the methiodide formed from them were sufficiently stable to permit isolation. The lower field signal from the two furan adducts is tentatively assigned to the endo form, since this appears generally to be the case with reactions of this type.[10b,12] In the reaction with cyclohexadiene, only one isomer (13a), thought to have the syn geometry shown (vide infra) was formed. With isoprene, regio-isomers 6a and 7a were formed (in a 1:2 ratio), as shown by the ^{31}P NMR spectrum.

Further characterization of the products of these addition reactions was accomplished by conversion into their methiodides, which in the cases of 5a and 14 (and the mixture of 8 and 9) were more amenable to elemental analysis. The salts 5a and 14 were also characterized by ^{13}C and ^{31}P (Scheme I) NMR spectral analysis.[13] The mixture of isomers 8 and 9 gave the expected ^{13}C spectrum and isolation of a small amount of 9 from the mixture by fractional crystallization allowed a complete ^{13}C assignment for both isomers.[13]

A few similar reactions were carried out with $PhP=CH_2$, generated in the same way. The diene trapping reactions gave products quite free of extraneous compounds. With isoprene, two regio-isomers (6b and 7b) were again obtained, in the ratio 9:1. The signals have not yet been associated with the proper regio-isomer. With 2,3-dimethylbutadiene, the adduct 4b was formed and this gave a methiodide (5b) having the expected ^{13}C NMR spectrum.[13] This methiodide was too light sensitive to give a good elemental analysis. With cyclohexadiene, a single adduct (13b)

SCHEME I

(δ ^{31}P values in parentheses)



was formed which, in the ^{13}C NMR spectrum,[13] showed couplings of 20.0 and 23.8 Hz for two of the sp^3 carbons, one of which is probably C7, and this indicates[6] the syn geometry shown.

With alcohols as trapping agents for $MeP{=}CH_2$, complex reaction products were formed, although that from methanol contained one major component having a ^{31}P NMR shift (δ 127 in MeOH) in close agreement with the reported value[14] for the expected product methyl dimethylphosphinite (Me_2POMe, δ ^{31}P (neat) 124).

Acknowledgement

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13. ^{13}C data (C atom, J_{PC} in Hz): for 5a; δ 7.9 (P-Me, 53.9), 17.5 (C6, 53.7), 20.1 (C4-Me, 2.24), 21.9 (C3-Me, 10.8), 25.0 (C2, 52.5), 26.7 (C5, 7.1), 118.0 (C3, 6.9), 138.8 (C4, 13.3): for 5b; δ 9.0 (P-Me, 53.4), 17.5 (C6, 52.3), 20.3 (C4-Me, 1.65), 21.9 (C3-Me, 10.6), 24.4 (C2, 52.2), 27.0 (C5, 6.7), 118.4 (C3, 7.0), 129.1 (C4, 13.6): for 8; δ 7.9 (P-Me, 53.8), 17.0 (C6 or C2, 50.5); 19.7 (C2 or C6, 53.1), 24.9 (C4-Me, 1.6), 25.2 (C5, 7.0), 111.8 (C3, 8.4), 136.1 (C4, 19.0): for 9; δ 8.1 (P-Me, 53.8), 15.9 (C6, 51.6), 20.4 (C5, 6.7), 23.8 (C2, 52.5), 26.3 (C3-Me, 10.6), 126.0 (C3, 6.2), 122.2 (C4, 15.3): for 13b; sp^3 carbons at δ 23.79 (C3 or C7, 20.0), 26.47 (C4 or C8, 3.5), 28.94 (C3 or C7, 23.8), 29.7 (C4 or C8, 0), 29.8 (C1, 11.5): for 14; sp^3 carbons at δ 8.78 (P-Me, 47.0), 10.28 (P-Me, 55.5), 19.1 (4.6), 24.0 (C1 or C3, 33.1), 24.3 (14.6), 28.0 (C1 or C3, 39.8), 28.2 (13.8); sp^2 carbons at 126.5 (C6, 9.9), 138.9 (C5, 13.9).
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