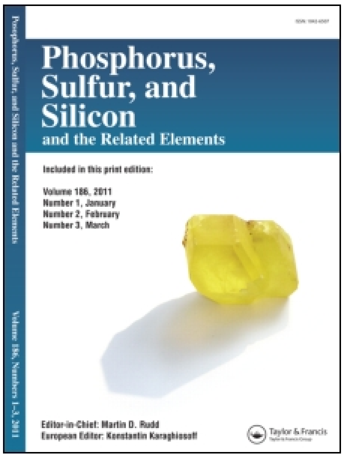

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CONCERNING THE STRUCTURE OF THE MALEIC ANHYDRIDE TRIETHYL PHOSPHITE CONDENSATE

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To cite this Article Denney, Donald B. and Denney, Dorothy Z.(1982) 'CONCERNING THE STRUCTURE OF THE MALEIC ANHYDRIDE TRIETHYL PHOSPHITE CONDENSATE', Phosphorus, Sulfur, and Silicon and the Related Elements, 13: 3, 315 — 317

To link to this Article: DOI: 10.1080/03086648208081190

URL: http://dx.doi.org/10.1080/03086648208081190

Phosphorus and Sulfur, 1982, Vol. 13, pp. 315–317
0308-664X/82/1303-0315/$06.50/0

CONCERNING THE STRUCTURE OF THE MALEIC ANHYDRIDE TRIETHYL PHOSPHITE CONDENSATE

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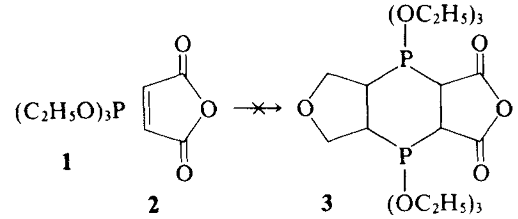
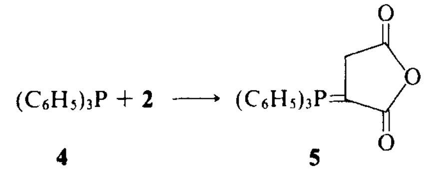
(*Received May 15, 1982*)

Triethyl phosphite and maleic anhydride react to give an ylide in which phosphorus has become bonded to an α-carbon of the anhydride and a proton has been transferred from that carbon to the adjacent α-carbon. The previously proposed phosphorane structure is incorrect.

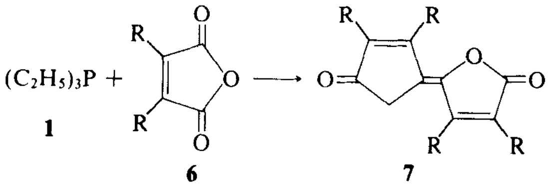
Recently it was reported that triethyl phosphite, **1**, and maleic anhydride, **2**, condense to give the novel phosphorane, **3**.[1] It was felt that this intriguing report deserved verification since other trivalent phosphorus compounds do not react in a similar manner. For example, the condensation of triphenylphosphine, **4**, with **2** has been shown to give the ylide, **5**.[2] Other reactions of maleic anhydrides, **6**, with triethyl phosphite have led to bifurane diones, **7**.[3] These products were found when the reactants were heated under reflux.



1 **2** **3**

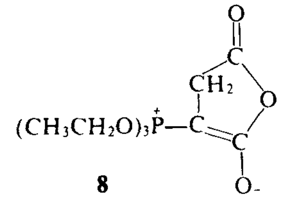


4 **5**



1 **6** **7**

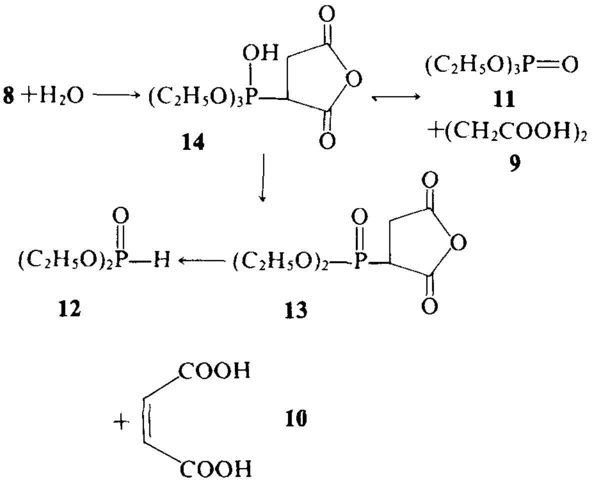
The condensation of **1** and **2** has now been investigated at room temperature in solution. Under these conditions the ^{31}P NMR resonance of triethyl phosphite at δ 138 disappears and is replaced by a new resonance at δ 41. This chemical shift is not in accord with that predicted for **3** which should probably be found around δ − 40 to −50.[4] Similarly, the ^{13}C NMR spectrum is not that expected for **3**. There are two carbonyl resonances one at δ 166.89 split by coupling to phosphorus, J = 28.7 Hz, and the other at δ 173.99 also split by coupling to phosphorus, J = 23.6 Hz. A doublet centered at δ 15.93 (J_{POCC} = 6.7 Hz) was shown to be due to the carbons of *methyl groups by single frequency off resonance decoupling*, SFORD. A resonance at δ 34.73 (J_{PCC} = 13.6 Hz) was shown to be due to a carbon of a methylene group and on the basis of the chemical shift it is assigned to a methylene group adjacent to a carbonyl group. Another resonance at δ 36.92 (J_{PC} = 247 Hz) is assigned to a carbon bearing no hydrogens and the large coupling constant suggests direct bonding to phosphorus. A resonance at δ 65.79 (J_{COP} = 6.1 Hz) is due to methylene carbons. These data are all in agreement with structure, **8**, as is the proton NMR spectrum which has typical absorptions for CH_3CH_2OP groups as well as a singlet at δ



8

3.2 which is assigned to the hydrogens of the methylene group adjacent to the carbonyl group. The corresponding adduct, **5**, has a resonance for methylene group hydrogens at δ 3.25.

Treatment of solutions of **8** with water led to a number of products. The formation of succinic, **9**, and maleic acids, **10**, was established by isolation. The ^{31}P NMR spectrum indicated that triethyl phosphate, **11**, diethyl phosphite, **12**, and a phosphonate, **13**, were present. These products can arise in the following manner. Attack by water on the phosphorus of **8** can yield **14** which then decomposes to **11** and **9** or **13**. Decomposition of **13** can account for the formation of **10** and **12**.



The complex ^1H NMR spectrum which was reported for **3** is probably that of a mixture of **8**, **9** and **11**. It was noted in this work that extreme care was required to suppress the formation of **9** and **11**.

EXPERIMENTAL

^{1}H NMR spectra were recorded with Varian T-60, A60A and FT 80 spectrometers. Chemical shift values are reported in parts per million relative to internal tetramethylsilane. ^{13}C and ^{31}P spectra were recorded with a Varian FT 80 spectrometer equipped with a variable-temperature broad band probe. In all cases nuclei that are deshielded relative to their respective standard are assigned a positive chemical shift. Most ^{13}C NMR spectra were obtained by using full proton decoupling, a 45° flip angle and 2-s repetition rate with no pulse delay. All ^{13}C chemical shifts are reported in parts per million relative to internal tetramethylsilane. ^{31}P NMR spectra were acquired using a 45° flip angle, a 1-s repetition rate with no pulse delay and with full proton decoupling. Chemical shifts are reported relative to external phosphoric acid (85%).

All manipulations were carried out under an atmosphere of argon. All solvents were freshly distilled and dried. All reagents were either distilled or recrystallized and all were subjected to analysis by NMR before being used.

Reaction of Triethyl Phosphite with Maleic Anhydride. In a typical 10 mm NMR tube experiment maleic anhydride (0.10 g, .001 mol) was dissolved in 1 mL of dichloromethane-d_2 and to this was added at 0°C triethyl phosphite (0.17 g, 0.001 mol) dissolved in 1 mL of dichloromethane-d_2. The ^{31}P NMR spectrum initially showed resonances at δ 138 and δ 41. After standing at room temperature for one hr the only resonance observable was at δ 41. At this time the ^{13}C NMR spectrum showed resonances at δ 15.93 (d, $J_{CCO_7} = 6.7$, —CH_3), δ 34.73 (d, $J_{CCP} = 13.6$, —CH_2—), δ 36.92 (d, $J_{CP} = 247$, P—C—), δ 65.79 (d, $J_{COP} = 6.1$, O—CH_2—), δ 166.89 (d, J_{CCP} or $J_{CCP} = 28.7$, C=O), δ 173.99 (d, J_{CCP} or $J_{CCCP} = 23.6$, C=O). The number of hydrogens bonded to each carbon was established by running a SFORD experiment. The ^{1}H NMR spectrum showed absorptions at δ 0.98 (d of t, $J_{HCCH} = 7.0$, $J_{HCCOP} = 0.8$, 9H), δ 3.80 (d of q, $J_{HCCH} = 7.1$, $J_{HCOP} = 8.2$, 6H). δ 3.2 (s, 2H). The infrared spectrum had strong absorptions at 1740 and 1820 cm^{-1}. At this time a small amount of water was added to the reaction mixture. After having been kept at room temperature for one hr, the ^{31}P NMR spectrum showed resonances at δ 17.0, 7.6 and −1.6. The absorption at δ 7.6 is a doublet, $J_{PH} = 694$.

In another experiment, to a solution of maleic anhydride (0.98 g, 0.01 mol) in dichloromethane (20 mL) was added triethyl phosphite (1.66 g, 0.01 mol) in dichloromethane (5 mL). One hour after the addition was completed the ^{31}P NMR spectrum showed essentially one absorption at δ 39 (external lock). Water was then added (0.5 g, 0.03 mol). After one hour, the ^{31}P NMR spectrum showed resonances at δ − 1.6, 7.6 and 22.3 (external lock). This solution was allowed to stand at room temperature for two days. A solid was formed which was separated by filtration. ^{1}H NMR (dimethyl sulfoxide-d_6) 2.47 (s), ^{13}C NMR (dimethyl sulfoxide-d_6) δ 28.97 and 193.84. Succinic acid dissolved in dimethyl sulfoxide-d_6 showed the following: ^{1}H NMR 2.41 (s), ^{13}C NMR δ 29.00 and δ 173.87. The supernatant liquid was concentrated and it was then dissolved in dimethyl sulfoxide-d_6, ^{1}H NMR δ 1.27 (t, 7.0), δ 2.45 (s), δ 4.04 (m), δ 5.70 (residual CH_2Cl_2), δ 6.27 (s). The resonance at δ 6.27 increased in size upon addition of maleic acid. A new resonance at δ 6.61 appeared upon the addition of fumaric acid.

ACKNOWLEDGMENT

This research has been supported by the Public Health Research Grant, GM26428. We also wish to thank the Mobil Chemical Co. for funds which aided in the purchase of NMR equipment.

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