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JMS Letters

Dear Sir,

Gas-phase Reactivity of $(CH_3O)_2P^+$ Phosphenium Ion Towards 2,3-Dimethylbuta-1,3-diene in a Quadrupole Ion Trap

Among the two-coordinated phosphorus cations, phosphenium ions (R_2P^+) have received particular attention by organic chemists in the last decade. The presence of a vacant π orbital and a lone electron pair confers on these amphoteric cationic species a high reactivity on organic substrates, as summarized in several reviews.[1] For instance, phosphenium ions are known to react as Lewis acids with phosphines to form stable adducts or as carbenoids with alkynes or dienes to give the corresponding unsaturated phosphorus heterocyclic compounds. However, most reactions in solution have been reported with phosphenium ions featuring at least one amido group to impart the necessary thermodynamic stabilization of the cationic center. The chemical behavior of phosphenium cations with other substituents such as RO has never been studied because of the insufficient π donor character of these groups.

Mass spectrometry provides a convenient way of forming even-electron cations in the gas phase and of studying their reactions with many substrates. Moreover, the intrinsic properties and reactions of ionic species are best studied in the gas phase in the absence of counter ions or solvent molecules. To the best of our knowledge, only two studies on the gas-phase chemistry of phosphenium cations have been reported. Hodges *et al.*[2] investigated by ion cyclotron resonance spectroscopy (ICR) the ion–molecule reactions between the $(CH_3O)HP^+$ and $(CH_3O)_2P^+$ phosphenium ions and trimethyl phosphite. Recently, the gas-phase reactivity of $(CH_3O)_2P^+$ ions with stereoisomeric diols has been studied by Thoen *et al.*[3] by Fourier transform ICR techniques.

In order to investigate the occurrence of cycloaddition reactions of phosphenium ions in the gas phase, we studied the reactions of the $(CH_3O)_2P^+$ ions with an activated diene, 2,3-dimethylbuta-1,3-diene (DMB). The $(CH_3O)_2P^+$ cations were generated from trimethyl phosphite (TMP) upon electron ionization (EI). A quadrupole ion trap (QIT) mass spectrometer, which is proving to be an effective device for studying ion–molecule reactions,[4] was chosen for this study. The ion isolation and MS^n capabilities of the QIT coupled with gas chromatography (GC) allowed the study of the reactions with DMB, introduced into the ion trap via the calibration gas inlet, and of the overall reactivity of the ionic species towards the neutral precursor[5] as it eluted from the GC column.

DMB was obtained from Aldrich with a stated purity of 98% and used as received. TMP was obtained from Fluka and diluted in pentane to a concentration of 100 ppm. The ion–molecule reactions were carried out with a QIT Varian Saturn 3 under the following conditions: 1 μl of a dilute solution of TMP was injected in the chromatograph in the splitless mode with the injector held at 185 °C. The GC column was held at 50 °C for 5 min and then ramped to 100 °C at 10 °C min^{-1} and held at the final temperature for 5 min. The data acquisition sequence was composed of (i) 70 eV EI of TMP, (ii) isolation of the phosphenium ion with a mass isolation window of 3 *m/z* and adjustments of the amplitude of the 1.05 MHz r.f. voltage applied to the ring electrode so as to store ions at a q_z value of 0.4, (iii) a reaction time of up to 50 ms with DMB (and neutral precursor) and (iv) ejection and detection (tandem mass spectrometry MS^2) of product ions using the mass-selective instability scan[6] and axial modulation[7] for improved resolution. Collision-induced dissociation (CID) experiments were performed using resonance excitation[8] by the application of a supplementary a.c. voltage to the end-cap electrode at an appropriate voltage. Triple mass spectrometric (MS^3) experiments using the software Toolkit were performed to characterize the ion–molecule reactions products.

The isolated phosphenium ions $(CH_3O)_2P^+$ (*m/z* 93) were allowed to react with DMB for 50 ms. The resulting ion–molecule reaction products are shown in Fig. 1. This spectrum (MS^2) shows that the $(CH_3O)_2P^+$ ions readily react with DMB to give a stable adduct at *m/z* 175 which corresponds in mass to the $[4 + 2^+]$ cycloaddition product. The suggested structure for the adduct (Scheme 1) relies on the results of Cowley *et al.*,[9] obtained in solution. They reported that the ^{31}P, ^{1}H and ^{13}C NMR data and the X-ray diffraction pattern of the adduct, which arises from reaction between the $(Me_2N)_2P^+$ cations and DMB, are entirely consistent with the 3-phospholenium ion structure.

In order to confirm the structure of the *m/z* 175 species, a CID spectrum was recorded. The spectrum shows that dissociation yields only two ions of *m/z* 93 and 143. The fragments correspond to the elimination of neutral species which are assigned to the retro-Diels–Alder reaction and to loss of methanol, as illustrated in Scheme 2. These fragmentations, which prove the covalently bound nature of the adduct and rule out any loosely bound structure, are consistent with the occurrence of $[4 + 2^+]$ cycloaddition yielding the formation of the 3-phospholenium cations.

In addition to the cycloaddition products, Fig. 1 displays other ions which are the result of reactions between phosphenium ions and the neutral precursor (TMP). In order to confirm its origin, these ions were isolated for 50 ms in the absence of DMB and the resulting ion–molecule reaction products are shown in Fig. 2. The spectrum contains five ion–molecule reaction products, at *m/z* 111, 125, 139, 141 and 217, which are the result of various reaction channels as summarized in Scheme 3.

As observed previously,[5] there are significant differences between the conditions in the QIT and those in an ICR cell. The formation of the ion–molecule reaction products at *m/z* 125, 139 and 217 has been reported previously by Hodges *et al.*[2] Nevertheless, the reaction conditions in the QIT differ sufficiently to produce other reaction products at *m/z* 111 and 141. The principal reaction between the mass-selected ion of *m/z* 93 and the neutral TMP is an addition reaction yielding a stable adduct at *m/z* 217. The $(CH_3O)_2P^+$ phosphenium cations also undergo a methyl cation transfer with TMP to give an ion at *m/z* 139. The three other product ions at *m/z* 111, 125 and 141 cannot be formed by ion–molecule reactions between *m/z* 93 and neutral TMP. The ion at *m/z* 111, which corresponds to the protonated dimethyl phosphite $[(CH_3O)_2P(OH_2)]^+$, is the result of addition of the background water to the *m/z* 93 ions. Note that such reactions have also been reported for the $[(CH_3O)_2P{=}O]^+$ phosphonium ion.[5,10] The formation of the protonated trimethyl phosphite at *m/z* 125 can be explained by means of MS^3 experiments. The isolated *m/z* 111 or 141 ions, generated from the mass-selected *m/z* 93, react with neutral TMP to give only one ion–molecule reaction product at *m/z* 125. In fact, the strong base TMP (proton affinity (PA) = 929 kJ mol^{-1})[11] is able to deprotonate both the protonated dimethyl phosphite (*m/z* 111) according to a nearly thermoneutral process and the *m/z* 141 ions which appear to correspond to the protonated trimethyl phosphate (PA = 891 kJ mol^{-1}).[11] Our findings, which clearly prove the origin of the *m/z* 125 ions, conflict

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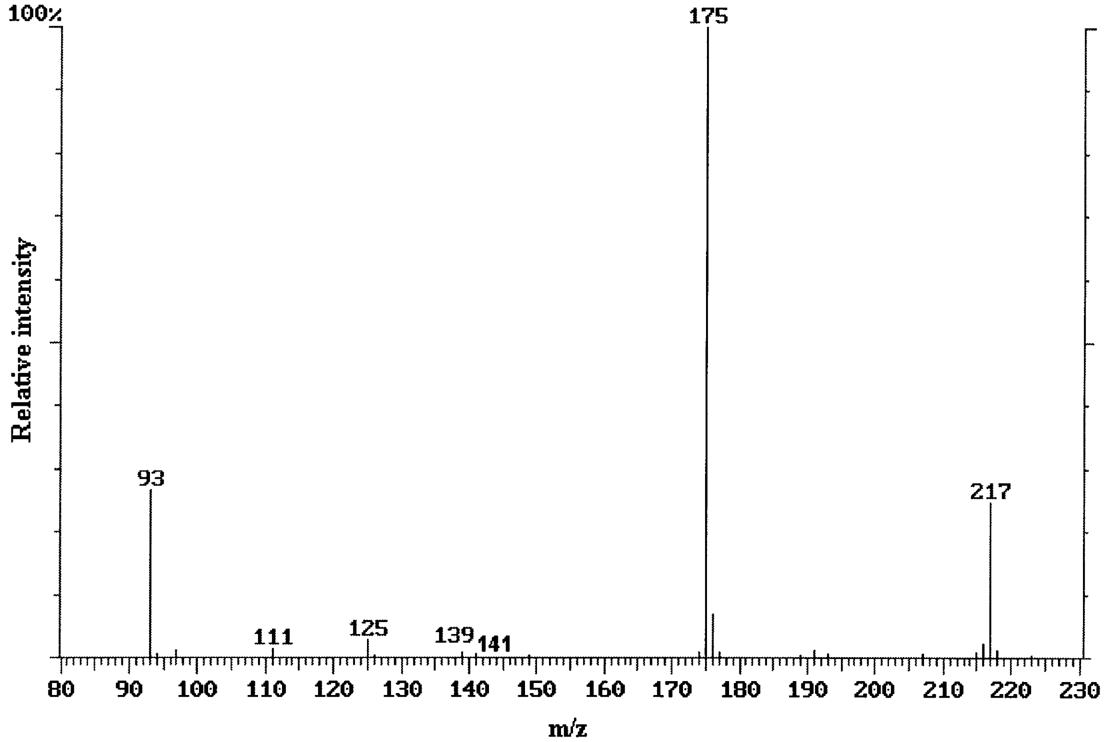
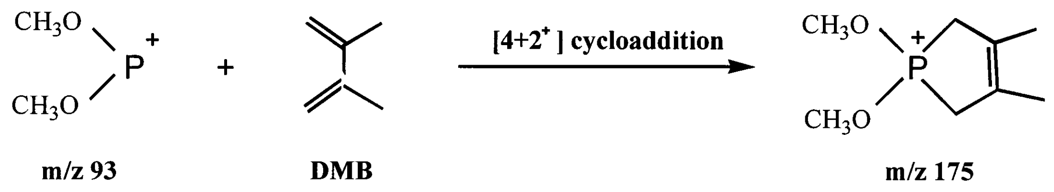


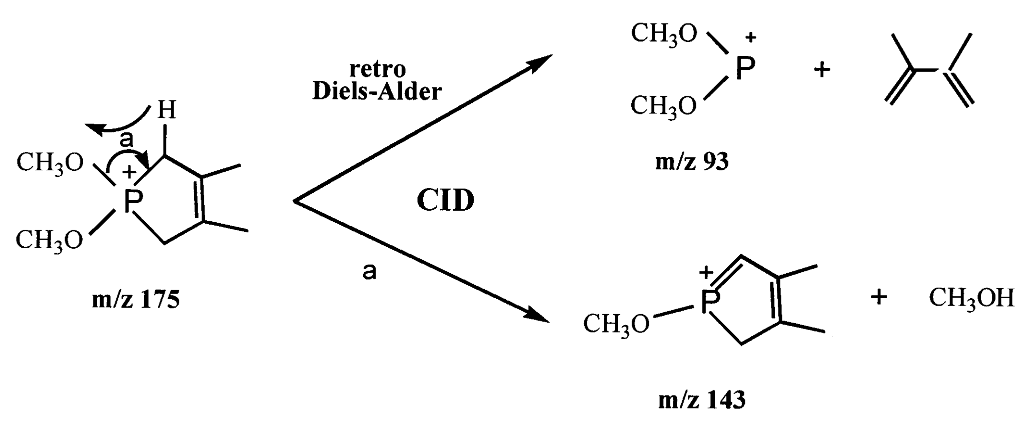
Figure 1. MS^2 product spectrum for the ion–molecule reactions of mass-selected *m*/*z* 93 ions with DMB for 50 ms.

with the assumption of Hodges *et al.*,[2] who suggested that protonated trimethyl phosphite was formed by proton transfer from the phosphenium ions (*m*/*z* 93). In order to confirm the structure of the *m*/*z* 141 ions, a reference protonated trimethyl phosphate was generated from the proton transfer reaction between the $(CH_3O)(OH)P{=}O^+$ ions obtained by EI-induced dissociation of the sample and the neutral trimethyl phosphate. Upon collisional activation, these ions were found to yield the same fragment ions as the *m*/*z* 141 ions shown in Fig. 2 (*m*/*z* 109 is the major CID product). This result strongly suggests that the *m*/*z* 141 ions and protonated trimethyl phosphate must have the same structure. The origin of the *m*/*z* 141 ions has been confirmed by MS^3 experiments. The MS^3 results show that the isolated *m*/*z* 217 and 139 ions generated from the mass-selected *m*/*z* 93 ions do not yield the formation of *m*/*z* 141 species. The formation of the *m*/*z* 141 ions might arise from a consecutive ion–molecule reaction of the highly reactive *m*/*z* 93 species with the neutral $(CH_3O)_2P(OH)$ which results from the proton transfer reaction between *m*/*z* 111 and TMP (Scheme 3).

In this study, the gas-phase reactivity of the $(CH_3O)_2P^+$ phosphenium ions towards both 2,3-dimethylbuta-1,3-diene



Scheme 1



Scheme 2

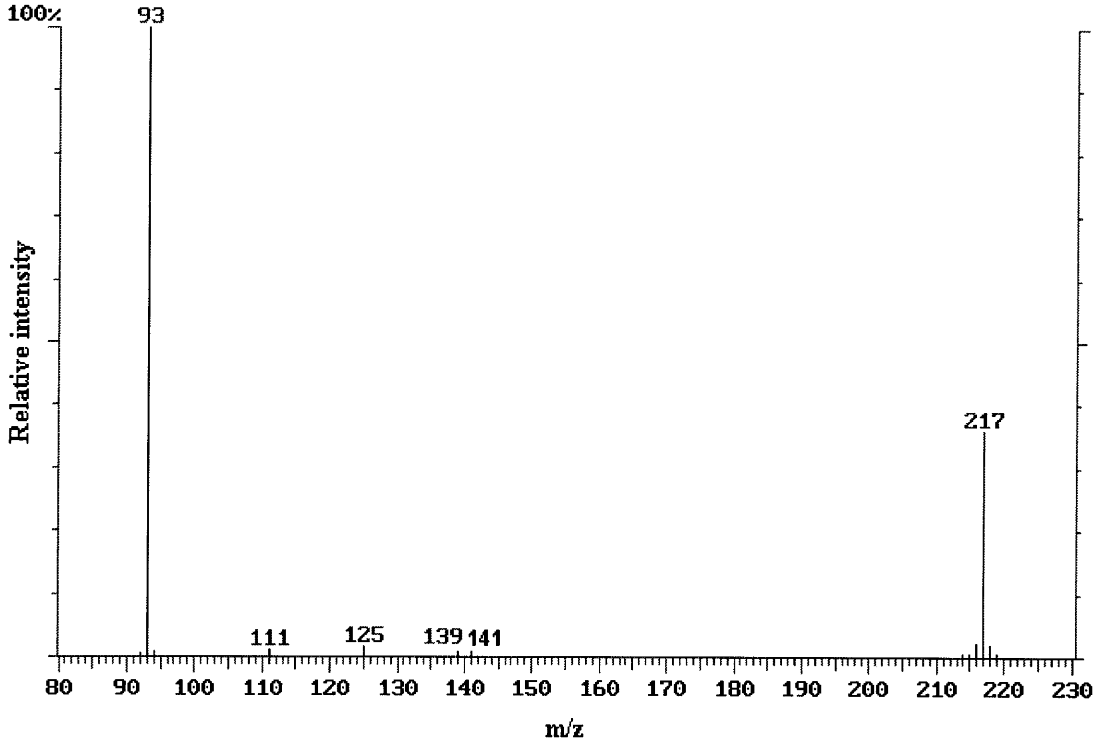
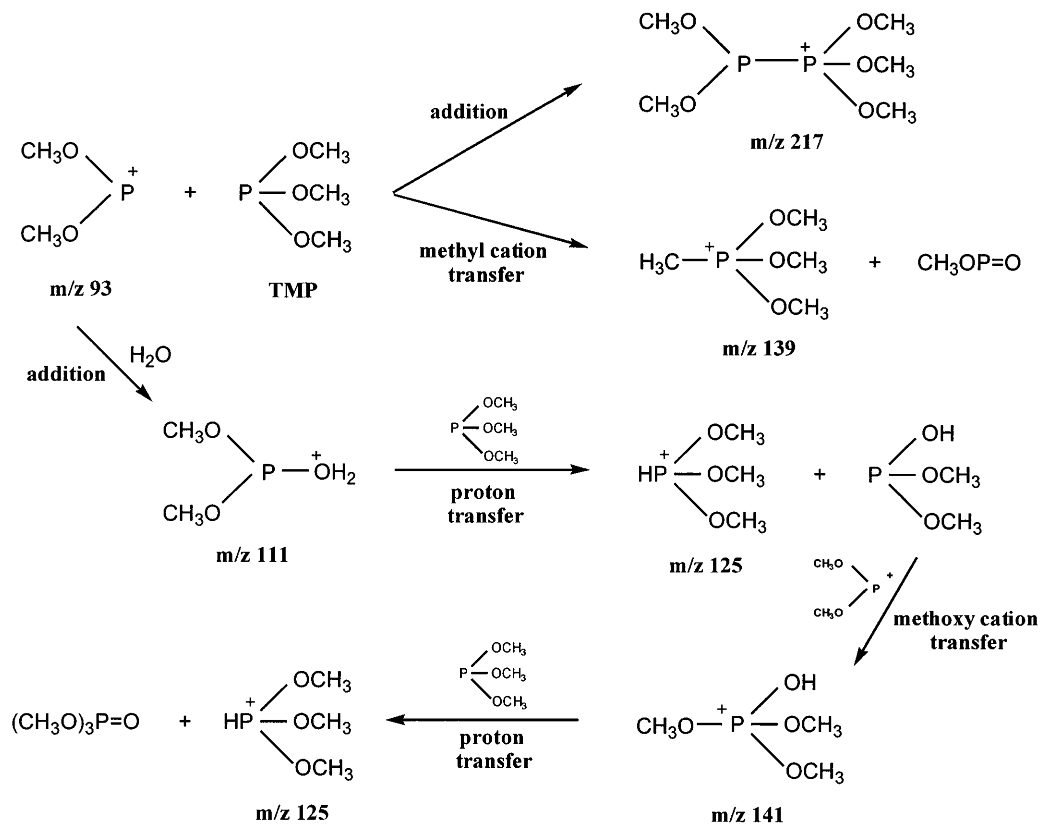


Figure 2. MS^2 product spectrum for the ion–molecule reactions of mass-selected *m/z* 93 ions with TMP for 50 ms.

and the neutral precursor trimethyl phosphite was carried out under GC/MS^n conditions. As observed in solution[1] for the nitrogen homologue $[(CH_3)_2N]_2P^+$, adduct formation is the major process which occurs when the *m/z* 93 ions are allowed to react with DMB or TMP. In addition, these highly reactive ionic species were found to undergo other ion–molecule reactions such as methyl cation transfer with TMP, adduct formation with residual water and methoxy cation transfer with



Scheme 3

dimethyl phosphite. Further work is in progress to investigate the reactivity of these phosphenium ions towards a variety of unsaturated organic substrates.

Yours,

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