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New phosphorus ylides in reactions of tertiary phosphines with phosphorylated quinone methide

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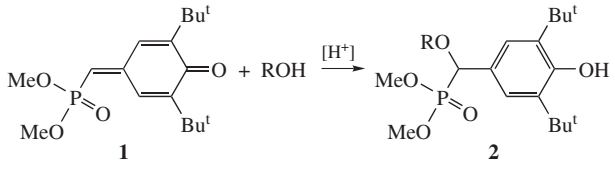
A series of new phosphonium ylides have been synthesized by the reaction of dimethyl-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidene)methylphosphonate with tertiary phosphines, the structure of dimethoxyphosphoryl-3,5-di-*tert*-butyl-4-hydroxyphenylmethylidene triphenylphosphorane has been confirmed by X-ray single crystal diffraction.

The reactions of phosphorylated quinone methides with nucleophilic reagents result in formation of more thermodynamically stable aromatic phenol systems. Such reactions proceed, as a rule, by the 1,6-addition mechanism.

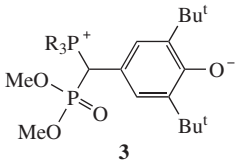
For example, dimethyl-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidene)methylphosphonate **1** reacts with alcohols in the presence of catalytic amounts of mineral acids to give corresponding phenols **2**.[1]



1 **2**

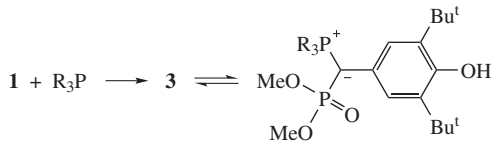
R = Me, Et, Pr^i, Bu

Phosphorus-containing nucleophiles were not previously examined in such reactions. Here, we report the reactions of phosphorylated quinone methide **1** with tertiary phosphines, in particular, triphenyl-, tributyl- and methyldiphenyl phosphines, carried out in order to obtain phenolate phosphabetaines **3**.



3

Phosphorylated quinone methide **1** with tertiary phosphines gives stable colourless crystalline products with high melting points. The structure of all products was proved by spectral methods and elemental analysis.[†] The absorption band of the quinone carbonyl group (1632 cm^{-1}) disappears in the IR spectra while the absorption band of the hydroxyl groups at 3150–3250 cm^{-1} of the crystalline products appears, the frequency of the phosphoryl group absorption band being shifted from 1248 to 1145–1150 cm^{-1}. The ^{31}P NMR spectra have two doublets of phosphonate and phosphonium phosphorus atoms due to their spin–spin coupling, observed at 16–22 and 28–34 ppm, respectively. Thus, spectral data give evidence for the formation of phosphonium ylides **4** rather than isomeric phenolate betaines **3**. The following scheme may be proposed with the C–H hydrogen atom of the quinine methide migrating in the course of the reaction towards oxygen atom of the phenolate anion.



4a PR$_3$ = PPh$_3$
4b PR$_3$ = PBu$_3$
4c PR$_3$ = PPh$_2$Me

The IR spectra of the products dissolved in acetonitrile reveal the sharp decrease of the intensity of the hydroxyl absorption band, thus giving evidence for the predominance of tautomeric form **3** in solution. As it was shown by X-ray single crystal diffraction (Figure 1),[‡] ylide tautomeric form is stabilized by strong intermolecular [O–H···O=P (*x*, *y*, *z* + 1)] hydrogen bonds, which lead to the formation of infinite chains along the *c*-axis: O–H 0.83(4), H···O=P 1.87(4), O···O=P 2.678(5) Å, ∠O–H···O 166.5°.

The carbon atom bearing a negative charge has a nearly planar configuration with the sum of valence angles of 359.92°. Typical of *sp*^{2}-hybridized carbon atom the P(3)–C(1) bond is eclipsed

[†] *Dimethyl-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidene)methyl-phosphonate* **1**: yield 76%, mp 105–107 °C. IR (*ν*/cm^{-1}): 1632 (C=O), 1584 (C=CH), 1248 (P=O), 1056, 1036 (POC). ^{31}P NMR ($CDCl_3$) *δ*: 18.26. ^{1}H NMR ($CDCl_3$) *δ*: 1.32 (s, 9H, CMe_3), 1.34 (s, 9H, CMe_3), 3.82 (s, 3H, MeO), 3.85 (s, 3H, MeO), 6.04 (m, 1H, PCH), 6.82 (s, 1H, C*H*=C–Bu^t), 7.99 (s, 1H, C*H*=C–Bu^t). Found (%): C, 62.01; H, 8.19; P, 9.72. Calc. for $C_{17}H_{27}O_4P$ (%): C, 62.58; H, 8.28; P, 9.51.

*Dimethoxyphosphoryl-3,5-di-*tert*-butyl-4-hydroxyphenylmethylidene triphenylphosphorane* **4a**: yield 67%, mp 128.7 °C. IR (*ν*/cm^{-1}): 1145 (P=O), 3200 (OH). ^{31}P NMR ($CDCl_3$) *δ*: 18.04 (d, $^2J_{P–P}$ 76.29 Hz), 27.91 (d, $^2J_{P–P}$ 76.29 Hz). Found (%): C, 71.43; H, 7.13. Calc. for $C_{35}H_{42}O_4P_2$ (%): C, 71.43; H, 7.14.

*Dimethoxyphosphoryl-3,5-di-*tert*-butyl-4-hydroxyphenylmethylidene tributylphosphorane* **4b**: yield 85%, mp 164 °C. IR (*ν*/cm^{-1}): 1148 (P=O), 3150 (OH). ^{31}P NMR ($CDCl_3$) *δ*: 22.65 (d, $^2J_{P–P}$ 85.45 Hz), 34.11 (d, $^2J_{P–P}$ 85.45 Hz). Found (%): C, 65.97; H, 10.23. Calc. for $C_{29}H_{54}O_4P_2$ (%): C, 65.90; H, 10.34.

*Dimethoxyphosphoryl-3,5-di-*tert*-butyl-4-hydroxyphenylmethylidene methyldiphenylphosphorane* **4c**: yield 92%, mp 155.4 °C. IR (*ν*/cm^{-1}): 1150 (P=O), 3250 (OH). ^{31}P NMR ($CDCl_3$) *δ*: 16.98 (d, $^2J_{P–P}$ 80.00 Hz), 34.09 (d, $^2J_{P–P}$ 80.00 Hz). Found (%): C, 68.52; H, 7.73. Calc. for $C_{30}H_{38}O_4P_2$ (%): C, 68.44; H, 7.60.

with the P(2)=O(5) bond resulting in a P···O=P contact shorter than the sum of the van der Waals radii. The P–C(1) bond lengths are equal within experimental errors and are much smaller than the P–Ph bond lengths.

Note that the synthesis of phosphorus ylides is usually very complicated while in the reported reaction they are obtained easily and with a good yield.

We are grateful to Dr. R. Fröhlich and Professor G. Erker for the opportunity to use X-ray facilities at the University of Münster.

‡ *X-ray crystal data for* **4a**: $C_{35}H_{42}O_4P_2$, $M = 588.63$, yellow crystal 0.10×0.10×0.03 mm, monoclinic, space group $P2_1/c$ (No. 14), $a = 9.378(1)$, $b = 33.812(1)$ and $c = 10.215(1)$ Å, $\beta = 93.21°$, $V = 3234.0(5)$ Å^3, $d_{calc} = 1.209$ g cm^{-3}, $\mu = 1.503$ mm^{-1}, empirical absorption correction ($0.864 \le T \le 0.956$), $Z = 4$, $\lambda = 1.54178$ Å, $T = 223$ K, ω and φ scans, 43628 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 5734 independent ($R_{int} = 0.103$) and 4239 observed reflections [$I \ge 2\sigma(I)$], 382 refined parameters, $R = 0.056$, $wR_2 = 0.140$, max. residual electron density 0.36 (–0.46) eÅ^{-3}, hydrogen atoms calculated and refined as riding atoms, except hydroxyl hydrogen which was revealed from difference Fourier map and refined isotropically. Data set for crystal **4a** was collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN,[2] absorption correction Denzo,[3] structure solution SHELXS-97,[4] structure refinement by full-matrix least-squares against F^2 using SHELXL-97,[5] graphics SCHAKAL.[6]

CCDC 713076 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2009.

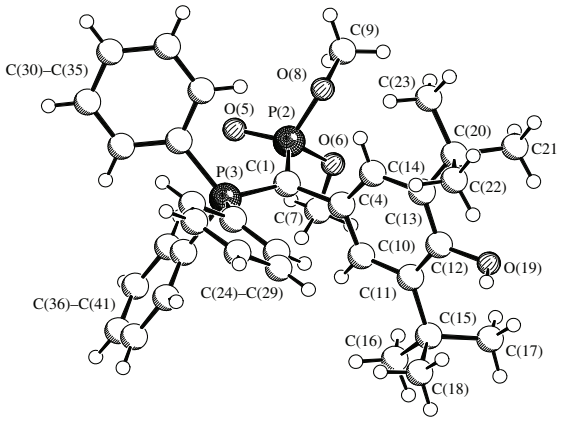


Figure 1 Molecular structure of ylide **4a**.

References

1 R. K. Ismagilov, V. V. Moskva, V. P. Arkhipov, A. E. Ivantsov and L. Yu. Kopylova, *Zh. Obshch. Khim.*, 1991, **61**, 387 (in Russian).
2 Z. Otwinowski and W. Minor, *Methods in Enzymology*, 1997, **276**, 307.
3 Z. Otwinowski, D. Borek, W. Majewski and W. Minor, *Acta Crystallogr.*, 2003, **A59**, 228.
4 G. M. Sheldrick, *Acta Crystallogr.*, 1990, **A46**, 467.
5 G. M. Sheldrick, *SHELX97. Programs for Crystal Structure Analysis*, University of Göttingen, 1997.
6 E. Keller, *SCHAKAL97. A Computer Program for the Graphical Representation of Molecular and Crystallographic Models*, University of Freiburg, 1997.

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