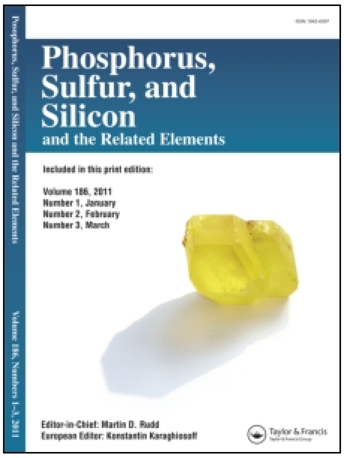

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REACTION OF PHOSPHORYLATED QUINONE METHIDES WITH TRIVALENT PHOSPHORYL COMPOUNDS

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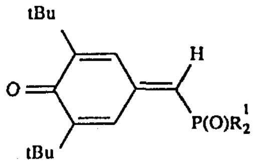
Abstract By reaction of bisphosphoryl quinone methides **2** with diethyl phosphite or diphenylphosphine oxide, depending on sterical requirements, the trisphosphorylderivatives **4a** and **4b** or **5** and **6** respectively, are formed. The latter reaction represents a new phosphorylation of an aromatic nucleus. With triethylphosphite and **1a** a stable ylide **8** was formed, while the betain **10**, expected from **2a** and triethylphosphite, immediately gave the trisphosphonate **4a** by splitting off ethylene. Attempts to prepare the trisphosphonate **11** gave the phosphate-phosphonate **12**, representing a new C-O-phosphoryl rearrangement.

INTRODUCTION

The surprisingly stable phosphonoquinone methides **1a** and **2a**, which we described recently$^{1)}$, simply added dialkylphosphite in 7-position: so **1a** reacts with diethylphosphite (DEP) to give the bisphosphonate **3a**; analogously **2a** affords the trisphosphonate **4a**$^{1)}$. Now we observed, that compounds of the type **1** and **2** show a different behavior to trivalent phosphorus compounds in dependence on the nature of R and the phosphorus species. This communication concerns the reaction of the quinone methides with DEP or diphenylphosphine oxide (DPP) and with triethylphosphite (TEP).

RESULTS

In a similar way as described for the synthesis of **4a** we have obtained the trisphosphoryl compound **4b**, having two phosphono- and a phosphinoxido-group in benzyl position, by reaction of **2a** and diphenylphosphine oxide (DPP), or from **2b**, prepared by dehydrogenation of **3b**, and DEP$^{2)}$. However, warming **2b** with DPP in ethanol/NaOEt did not give the expected **4**-analogous trisphosphoryl compound, but surprisingly **5b** was formed, a species having one phosphoryl group instead of the tert.-butyl group in the aromatic ring. The bisphosphine oxide **2c**, prepared from **3c** and PbO_2, behaved similiarly: warming with DPP afforded **5c**, while **6** was formed from **2c** and DEP. This unexpected reaction, proceeding under mild alcaline conditions, represents a new phosphorylation of an aromatic nucleus. The primary step of the reaction probably is a direct attack of the phosphoryl compound in 3-position, followed by splitting off isobutene. The latter could be identified clearly. The pathway of the reactions mentioned certainly depends on sterical requirements.



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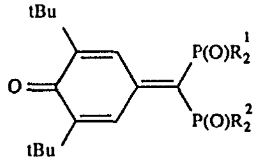

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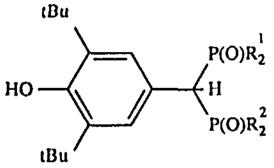

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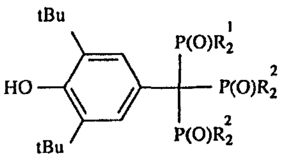

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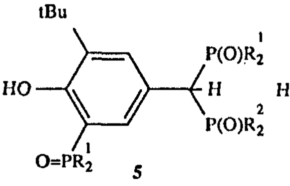

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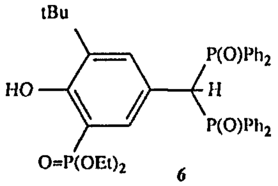
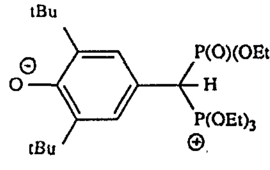


6

1 - 5	a	b	c
R^1	OEt	Ph	Ph
R^2	OEt	OEt	Ph

The phosphonoquinone methides **1a** and **2a** showed a different behavior to TEP in dependence on the substrate, too. So, **1a** and TEP formed an adduct, having not the expected structure of the betaine **7**, but of the ylide **8**, which could be proved unambigously. Solvolysis of the surprisingly stable **8** gave **3a**.



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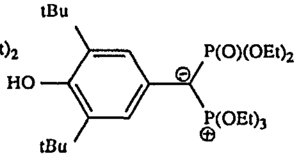

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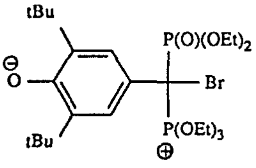

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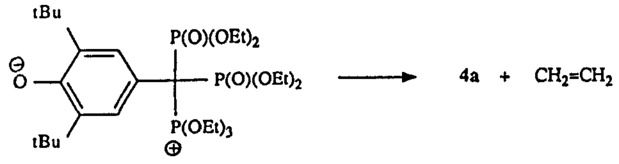
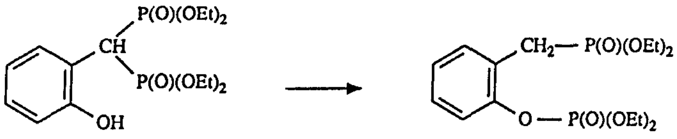
By bromination of **8** the bromoderivative **9** was expected, but it showed to be instable: by elimination of HBr the bisphosphonoquinone methide **2a** was formed and HBr was trapped by unchanged **8** to give the bisphosphonate **3**.

From the bisphosphonoquinone methide **2a** and TEP the betaine **10** should be formed. However, even under inert conditions, only the trisphosphonate **4a** was obtained. The ethylene to be released in the course of direct conversion of the primarly formed **10** into **4a** could be detected unambigously$^{3)}$.



10

Bis- and trisphosphorylderivatives of the type **3** and **4** are stable compounds, we have never observed rearrangements of the phosphoryl group to the phenolic hydroxyl group. The trisphosphorylderivatives **5** and **6** are formed clearly via direct aryl phosphorylation and not by rearrangement of a previosly formed **4**-analogous trisphosphoryl compound.



11 **12**

On the other hand, attempts to prepare the o-hydroxy-benzyl bisphosphonate **11**, starting from different educts, always led to **12** only$^{4)}$. This reaction presents a new C-O-phosphoryl group rearrangement, a kind of "phenylogue" analogon of known phosphoryl group rearrangements, e.g. of 1-hydroxyethane-1,1-bisphosphonic ester.$^{5)}$

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