Reactions of the Monomeric Metaphosphate Anion Generated from Different Sources

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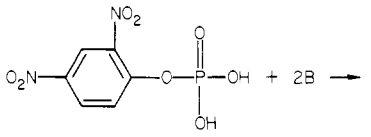
Abstract: The reactions of 0.2 M acetonitrile solutions of 2,4-dinitrophenyl dihydrogen phosphate and *erythro*-1-phenyl-1,2-dibromopropylphosphonic acid containing 2 molar equiv of diisopropylethylamine have been studied at 25 °C by means of ^{31}P NMR spectrometry at 145.7 MHz. The phosphate and phosphonate dianions generate monomeric metaphosphate anion, PO_3^-, at different rates. In the absence of added nucleophiles, the phosphate-derived metaphosphate produces *cyclic* trimetaphosphate, while the phosphonate-derived metaphosphate produces *acyclic* linear and branched polymetaphosphates. The monomeric metaphosphate anion from the slower phosphate decomposition adds to unreacted starting material and gives aryl pyrophosphate, which accepts more metaphosphate to yield aryl tripolyphosphate and finally cyclic trimetaphosphate by an intramolecular addition–elimination mechanism. The metaphosphate from the much faster phosphonate fragmentation does not encounter much unreacted starting material and, hence, undergoes genuine PO_3^- polymerization. Decomposition of the phosphonate in the presence of 4-nitrophenyl or 2,4-dinitrophenyl phosphate produces the corresponding aryl pyrophosphate $ArOP(O_2^-)O{\cdot}PO_3^{2-}$, and smaller amounts of acyclic polymetaphosphates. In the presence of 2 molar equiv of *tert*-butyl alcohol or phenol, the metaphosphate from both sources produces alkyl or aryl phosphates; however, no enol phosphate is observed in either case in the presence of acetophenone or ethyl pyruvate under comparable conditions. Ethyl acetoacetate as nucleophile produces <1% and ~2% of enol phosphate in the decomposition of phosphate and phosphonate, respectively. The highly enolic 1,3-cyclohexanedione (dihydroresorcinol) is converted into the enol phosphate, 3-oxo-1-cyclohexenyl phosphate, to an extent of ~80% as a result of the decomposition of both phosphate and phosphonate. It is concluded that when enol phosphates are observed in reactions of carbonyl compounds with metaphosphate anion sources, the enol phosphates are derived from the enol tautomer of the carbonyl compound. Analogous studies have been carried out with the monomethyl esters of the same phosphate and phosphonate. The phosphodiester anion is stable under conditions which slowly generate monomeric methyl metaphosphate from the phosphonate methyl ester anion.

Introduction

The monomeric metaphosphate anion, PO_3^-, which was first proposed as a reaction intermediate in aqueous solution,[2] has recently been observed in the gas phase by the technique of negative-ion chemical ionization mass spectrometry.[3] Mass spectrometry has also disclosed the formation of metaphosphoric acid and of monomeric methyl metaphosphate, CH_3OPO_2, via both thermal and electron-impact processes.[4] These same authors[4] have summarized the extensive preexisting literature on mass spectrometry of organophosphorus compounds which provides convincing evidence for the facile generation of these, and other, monomeric metaphosphate species in the gas phase.

Over the last 20 years, the formation and the reactivity of the metaphosphate anion have attracted much attention, partly owing to the possible implications of the subject in biochemistry.[5] The present study is concerned with two reactions which seem capable of generating the metaphosphate anion in aprotic solvents, namely, the decomposition of 2,4-dinitrophenyl phosphate (eq 1)[6] and of *erythro*-1-phenyl-1,2-dibromopropylphosphonate (eq 2).[7,8]



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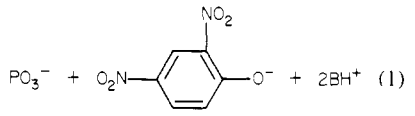

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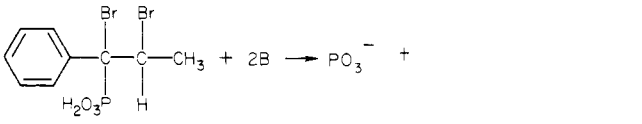

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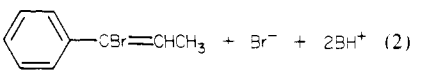

(2)

In our previous work, the reactions of 1 mol of the phosphoric acid derivative, **1**, and 2 mol of a hindered tertiary amine, diisopropylethylamine, were carried out in acetonitrile solution in the absence of added nucleophiles and in the presence of limited amounts of alcohol and water.[6] In an investigation by Satterthwait and Westheimer,[7c] the reaction of 1 mol of the phosphonic acid derivative, **2**, and ca. 80 mol of a hindered secondary amine,

(1) Research supported by Grant CHE79-04985 from the National Science Foundation.

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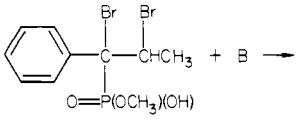
Table I. Decomposition of 2,4-Dinitrophenyl Dihydrogen Phosphate, *erythro*-1-Phenyl-1,2-dibromopropylphosphonic Acid, and Methyl Hydrogen *erythro*-1-Phenyl-1,2-dibromopropylphosphonate in the Presence of a Hindered Tertiary Amine at 25 °C

expt no.	added reagent	results[a]
	$2,4\text{-}(NO_2)_2C_6H_3OPO_3H_2$ + 2[$(CH_3)_2CH]_2NC_2H_5$; 0.2 M Solution in CH_3CN[b,c]	
1	none	$c\text{-}P_3O_9^{3-}$
2	none[d]	$2,4\text{-}(NO_2)_2C_6H_3OP(O_2^-)OPO_3H^-$ + $c\text{-}P_3O_9^{3-}$
3	$(CH_3)_3COH$	$(CH_3)_3COPO_3H^-$
4	C_6H_5OH	$C_6H_5OPO_3H^-$
5	$C_6H_5COCH_3$	$c\text{-}P_3O_9^{3-}$ [e,f]
6	$CH_3COCO_2C_2H_5$	$c\text{-}P_3O_9^{3-}$ [e]
7	$CH_3COCH_2CO_2C_2H_5$	$c\text{-}P_3O_9^{3-}$ [e]
8	1,3-cyclohexanedione	3-oxo-1-cyclohexenyl phosphate (ca. 80%)
	erythro-$CH_3C(H)(Br)C(C_6H_5)(Br)PO_3H_2$ + 2[$(CH_3)_2CH]_2NC_2H_5$; 0.2 M Solution in CH_3CN[c,g]	
9	none	linear-branched $(PO_3^-)_n$
10	$(CH_3)_3COH$	$(CH_3)_3COPO_3H^-$
11	C_6H_5OH	$C_6H_5OPO_3H^-$
12	$C_6H_5COCH_3$	linear-branched $(PO_3^-)_n$
13	$CH_3COCO_2C_2H_5$	linear-branched $(PO_3^-)_n$
14	$CH_3COCH_2CO_2C_2H_5$	$CH(CO_2C_2H_5)=C(CH_3OPO_3H^-$ (ca. 2%) + linear-branched $(PO_3^-)_n$
15	1,3-cyclohexanedione	3-oxo-1-cyclohexenyl phosphate (ca. 80%)
16	$2,4\text{-}(NO_2)_2C_6H_3OPO_3H^-$	$2,4\text{-}(NO_2)_2C_6H_3OP(O_2^-)OPO_3H^-$ (ca. 35%) + linear-branched $(PO_3^-)_n$
17	$4\text{-}NO_2C_6H_4OPO_3H^-$	$4\text{-}NO_2C_6H_4OP(O_2^-)OPO_3H^-$ (ca. 35%) + linear-branched $(PO_3^-)_n$
	$2,4\text{-}(NO_2)_2C_6H_3OPO_3H_2$ + 2[$(CH_3)_2CH]_2NC_2H_5$; 0.2 M Solution in the Ketone[b]	
18	$C_6H_5COCH_3$	$c\text{-}P_3O_9^{3-}$ [e,f]
	erythro-$CH_3C(H)(Br)C(C_6H_5)(Br)PO_3H_2$ + 2[$(CH_3)_2CH]_2NC_2H_5$; 0.2 M Solution in the Ketone[g]	
19	$C_6H_5COCH_3$	$CH_2=C(C_6H_5)OPO_3H^-$ (ca. 2%) + linear-branched $(PO_3^-)_n$
20	$CH_3COCH_2CO_2C_2H_5$	$CH(CO_2C_2H_5)=C(CH_3)OPO_3H^-$ (ca. 20%) + linear-branched $(PO_3^-)_n$
	erythro-$CH_3C(H)(Br)C(C_6H_5)(Br)P(O)(OCH_3)(OH)$ + [$(CH_3)_2CH]_2NC_2H_5$; 0.2 M Solution in CH_3CN[h]	
21	none	linear $(CH_3OPO_2)_n$
22	$(CH_3)_3COH$	$(CH_3)_3COP(O)(OCH_3)O^-$
23	$C_6H_5COCH_3$	$CH_2=C(C_6H_5)OP(O)(OCH_3)O^-$ (ca. 10%)[i] + linear $(CH_3OPO_2)_n$
24	1,3-cyclohexanedione[j]	methyl 3-oxo-1-cyclohexenyl phosphate (ca. 90%)

[a] Small amounts of $H_2PO_4^-$ resulting from inadvertent hydrolysis are omitted. [b] Products observed after 36 h, unless otherwise specified. [c] Two molar equivalents of the reagent were added per mole of phosphate or phosphonate. [d] 0.05 M CH_3CN solution observed after 4 h. [e] No enol phosphate was detected as a metastable intermediate at any stage of the reaction. [f] An authentic sample of 1-phenyl-1-ethenyl phosphate was shown to be stable under these conditions. [g] Products observed after 1 h. [h] Products observed after 24 h, when the decomposition of the phosphonate was about 65% complete. [i] Other ^{31}P NMR signals, possibly due to methyl 1-phenyl-2-bromo-1-propenylphosphonate resulting from dehydrobromination, were also detected. [j] At 70 °C for 24 h.

2,2,6,6-tetramethylpiperidine, was carried out with a large excess of acetophenone as the nucleophilic reagent. The solvent in that investigation[7c] was a 3:1 v/v mixture of the ketone and amine. In order to compare the behavior of the metaphosphate anion generated from these two different sources, **1** and **2**, we have now studied the reactions of the phosphate and the phosphonate under identical conditions, i.e., 0.2 M acetonitrile solutions containing 2 mol equiv of diisopropylethylamine and limited amounts of alcohols, phenols, ketones, or ketoesters. Our results suggest that when enol phosphates are observed in reactions of carbonyl compounds with metaphosphate anion sources in solution, the enol phosphates are derived from the enol tautomer of the carbonyl compound. This conclusion is at variance with that reached by Satterthwait and Westheimer,[7c] who, however, worked under somewhat different experimental conditions.

Monomeric methyl metaphosphate, CH_3OPO_2, has also been generated by a pyrolytic reaction,[9a-c] and more recently by fragmentation of methyl *erythro*-1-phenyl-1,2-dibromopropylphosphonate (**3**),[9d] eq 3. The latter investigation[9d] was carried



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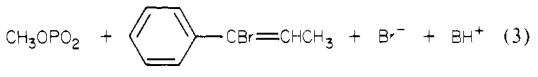

out under conditions analogous to those employed by the same authors in their study of the corresponding dibasic acid **2**. The methyl metaphosphate is significantly more difficult to generate, but much more reactive than the metaphosphate anion. Monomeric methyl metaphosphate lacks the potential biochemical relevance of the monomeric metaphosphate anion, but it is of considerable mechanistic interest, and we have included the methyl phosphonate, **3**, as well as methyl 2,4-dinitrophenyl phosphate (**4**) in the present study.

Results and Discussion

The results of this study are summarized in Table I. The course of the reactions was followed by ^{31}P NMR spectrometry at 145.7 MHz, and the pertinent data are given in Table II. The structural assignments are supported and complemented by ^1H NMR spectrometry. In questionable cases, the products of the reaction were isolated and were also prepared by independent procedures as described in the Experimental Section. Some of the reactions were carried out at higher concentrations (up to 1.5 M) in acetonitrile, and with different mole ratios of nucleophilic reagent to metaphosphate anion source (5:1), but these variations did not seem to alter the picture presented in Table I. There is little doubt that the anions derived from the phosphate and the phosphonate are the sources of the metaphosphate anion, since solutions of these compounds are reasonably stable in the absence of the hindered tertiary amine.

Experiments 1 and 9 in Table I disclose a significant difference in the products of the decompositions of the aryl phosphate **1** and the β-halophosphonate **2** in the absence of added nucleophiles. Under these conditions, the phosphate produces cyclic trimetaphosphate, $c\text{-}P_3O_9^{3-}$ (**5**), as the sole detectable product in a relatively slow reaction. The phosphonate, on the other hand, gives rise to acyclic linear-branched polymetaphosphates **6**.

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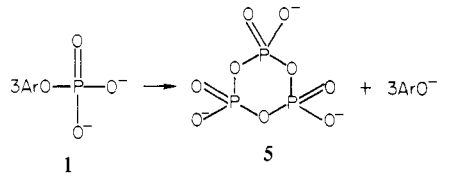

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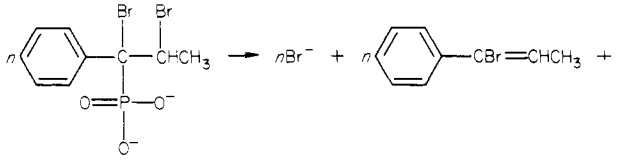

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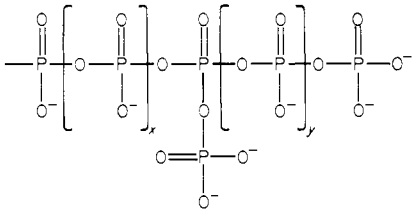

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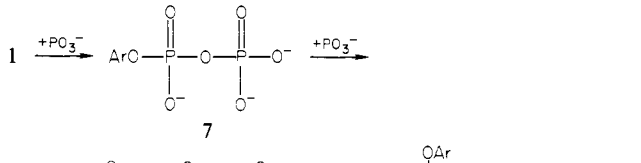
The structure of the cyclic trimetaphosphate **5** is based on documentation already discussed.[6] The structure of the acyclic linear-branched polymetaphosphate **6** is based on the data of Glonek, Van Wazer, and their co-workers.[10] This type of product has also been observed by Satterthwait and Westheimer[7c] in one of their reactions. We attribute the difference in the behavior of anions derived from phosphate **1** and phosphonate **2** to differences in the rate at which the metaphosphate anion is generated from the two sources in acetonitrile solution. The phosphate decomposes at a relatively slow rate, and the PO_3^- anion interacts with unreacted starting material. The resulting aryl pyrophosphate **7** accepts a second PO_3^- anion to give the linear aryl tripolyphosphate **8**. This intermediate has a highly electrophilic P_α-center and is sterically disposed to undergo intramolecular cyclization by an addition–elimination mechanism, presumably via an oxyphosphorane intermediate **9**. The phosphonate decomposes at a relatively fast rate, and the PO_3^- anion, finding little or no unreacted starting material, undergoes a polymerization reaction $nPO_3^- \rightarrow (PO_3^-)_n$.



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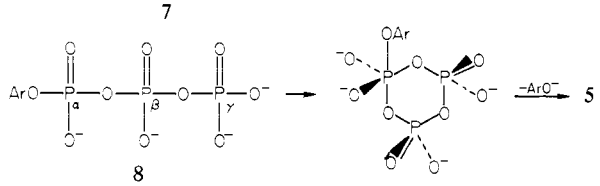

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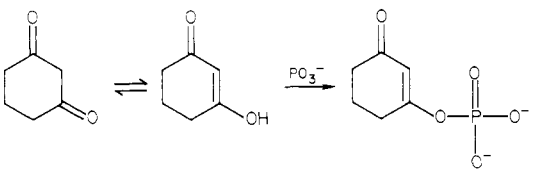
This interpretation is supported by the results of expt 16 in Table I. When phosphonate **2** is allowed to decompose in the presence of phosphate **1**, about one-third of the PO_3^- anion is trapped as aryl pyrophosphate **7**. The remaining PO_3^- anion appears as acyclic polymetaphosphate **6**. Analogous results are observed in the presence of 4-nitrophenyl phosphate (expt 17). The decomposition of phosphate **1** and phosphonate **2** in the presence of alcohols or phenols leads to the same type of products, i.e., the alkyl (**10**) or aryl (**11**) phosphates, respectively; *cf.* expts 3, 4, 10, and 11. We assume that the decompositions of the phosphate **1** and the phosphonate **2** are the rate-limiting steps in these reactions, and that alcohols, even the relatively hindered *tert*-butyl alcohol, and phenols are sufficiently nucleophilic to trap virtually all the PO_3^- anion as the corresponding phosphomonoester. There is no evidence for the formation of significant amounts of by-products in these reactions (traces of inorganic phosphate observed in all cases are attributed to hydrolysis by adventitious moisture).

The decomposition of phosphate **1** and phosphonate **2** in the presence of acetophenone or ethyl pyruvate does not alter the type of products that are formed when the same reactions are carried out in the absence of the carbonyl compounds; cf. expts 5, 6, 12, and 13. In none of these reactions could we detect enol phosphates. To exclude the possibility that 1-phenylethenyl phosphate (**12**) is actually produced in expts 5 and 12, but decomposes too rapidly for detection, this enol phosphate was prepared by an independent route.[11] 1-Phenylethenyl phosphate proved to be stable under the conditions of expts 5 and 12.

No enol phosphate can be detected from the decomposition of phosphate **1** in the presence of ethyl acetoacetate, expt 7. However, a very small amount, ca. 2% of 1-methyl-2-carbethoxyethenyl phosphate (**13**), is detected in the corresponding decomposition of the phosphonate **2**, expt 14. Most of the product, however, is the acyclic linear-branched polymetaphosphate. The most reasonable hypothesis is that the enol phosphate originates from the addition of the PO_3^- anion to the enol tautomer of the carbonyl compound, and that the keto tautomer is not reactive toward the monomeric metaphosphate anion. To test this hypothesis, we allowed the phosphate **1** and the phosphonate **2** to decompose in the presence of 1,3-cyclohexanedione, expts 8 and 15. This highly enolic β-diketone ("dihydroresorcinol") is, indeed, converted into the enol phosphate, 3-oxo-1-cyclohexenyl phosphate (**14**), as the major reaction product (80% of the theory).



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3-Oxo-1-cyclohexenyl phosphate (**14**) proved to be too unstable to survive purification steps. However, its formation is supported by comparisons of spectral data with data obtained from the more stable methyl 3-oxo-1-cyclohexenyl phosphate (**15**) prepared as described below.

From the data so far presented, we conclude that the metaphosphate anion generated from different sources reacts equally well with a given nucleophile, e.g., alcohols, phenol, or enol functions. However, in the case of carbonyl compounds with a relatively low enol content in the medium employed, other competing reactions of the PO_3^- anion may totally or partially obscure the tendency of this ion to add to the enol hydroxyl group.

In another set of experiments, the anions derived from phosphate **1** and from phosphonate **2** were allowed to decompose in a liquid carbonyl compound as the solvent. Owing to the relatively slow rate of decomposition of phosphate **1**, this type of experiment was feasible only in the case of acetophenone. With ethyl pyruvate and ethyl acetoacetate, amine-catalyzed condensations of the carbonyl compound interfered with the observation of the desired metaphosphate reaction. The faster decomposition of phosphonate **2** allows an examination of this reaction in acetophenone and in ethyl acetoacetate, but not in ethyl pyruvate. As seen from expts 18 and 19, no enol phosphate and only 2% of enol phosphate can be observed from phosphate **1** and phosphonate **2**, respectively, in the presence of acetophenone. Experiment 20 shows that a substantial amount of enol phosphate (ca. 20%) is observed when

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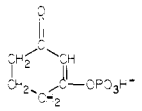
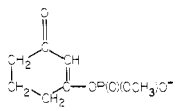
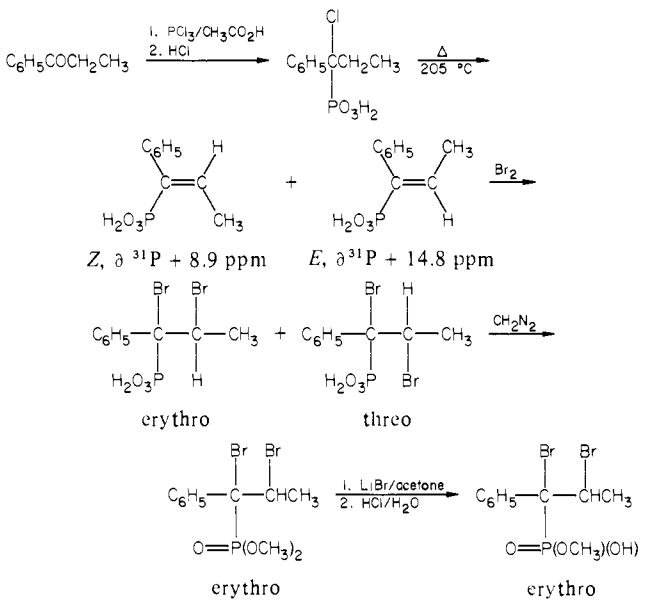
(11) Hata, T.; Yamada, K.; Futatsugi, T.; Sekine, M. *Synthesis* **1979**, 189.

Table II. ^{31}P NMR Chemical Shifts of Reactants and Products in the Decomposition of Aryl Phosphates and 1,2-Dibromophosphonates[a]

no.	compound	$\partial^{31}P$, ppm[a]
1	$2,4\text{-}(NO_2)_2C_6H_3OPO_3H^-$	−3.8 (s)
2	*erythro*-$CH_3C(H)(Br)C(C_6H_5)(Br)PO_3H^-$	+9.8
3	*erythro*-$CH_3C(H)(Br)C(C_6H_5)(Br)P(O)(OCH_3)O^-$	+9.2
5	*c*-$P_3O_9^{3-}$	−22.8 (s)
6	linear-branched $(PO_3^-)_n$	ca. −10[b] (m) ca. −25 (m) ca. −35 (m)
16	linear $(CH_3OPO_2)_n$	ca. −12[b] (m) ca. −23 (m)
7	$2,4\text{-}(NO_2)_2C_6H_3OP(O_2^-)OPO_3H^-$	−9.5 (m); −18.6 (m)
7A	$4\text{-}NO_2C_6H_4OP(O_2^-)OPO_3H^-$ $H_2PO_4^-$	−10.4 (m); −16.8 (m) +1.0 (s)
10	$(CH_3)_3COPO_3H^-$	−2.8 (s)
17	$(CH_3)_3COP(O)(OCH_3)O^-$	−3.8 (m)
11	$C_6H_5OPO_3H^-$	−5.4 (s)
12	$CH_2=C(C_6H_5)OPO_3H^-$	−5.0 (s)
18	$CH_2=C(C_6H_5)OP(O)(OCH_3)O^-$	−5.4 (m)
13	$CH(CO_2C_2H_5)=C(CH_3)OPO_3H^-$	−5.3 (s)
14		−6.5 (s)
15		−7.8 (m)

[a] From 85% H_3PO_4 = 0. Positive values are downfield from the reference; s = singlet; m = multiplet. The values given are those observed under the conditions of the reactions described in Table I. [b] Multiplets centered approximately at these values.

Scheme I

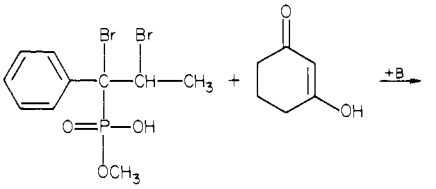


phosphonate **2** is allowed to decompose in ethyl acetoacetate as solvent.

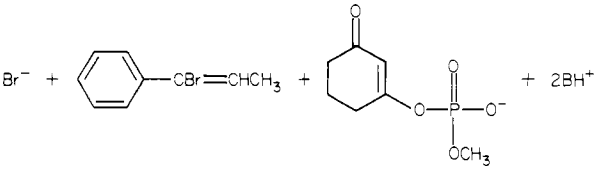
A comparison between expts 12 and 19 discloses that, with the same metaphosphate anion source, i.e., the phosphonate **2**, more enol phosphate is obtained in acetophenone as solvent than in a solution of the ketone in acetonitrile as solvent. The effect is more marked in the case of ethyl acetoacetate; cf. expts 14 and 20. These results would be expected from an increase in the amount of enol present in the pure ketone.

Several reactions were carried out with methyl *erythro*-1-phenyl-1,2-dibromopropylphosphonate (**3**) in acetonitrile solutions. The results are consistent with a much lower decomposition rate of the methyl phosphonate monoanion vs. the phosphonate dianion, and a higher rate of reaction of monomeric methyl metaphosphate vs. the metaphosphate anion.[7d,9d] The methyl phosphonate **3** generates linear polymethylmetaphosphate (**16**) in the absence of added nucleophiles (expt 21), and methyl *tert*-butyl phosphate (**17**) in the presence of *tert*-butyl alcohol (expt 22). Experiments 23 and 12 disclose that significantly more (10%) methyl 1-phenylethenyl phosphate (**18**) is obtained from the methyl phosphonate monoanion than was the case in the reaction of the phosphonate dianion **2** (both in acetonitrile solution with acetophenone as nucleophile). In both cases, the keto ⇌ enol equilibrium is presumably the same, and should be reestablished at a faster rate than the rate of reaction of monomeric methyl metaphosphate with the enol tautomer of acetophenone. Hence, the 10% enol phosphate **18** in expt 23 is reasonable. On the other hand, the less reactive metaphosphate anion seems to prefer to polymerize rather than react with acetophenone enol in dilute acetonitrile solution.

Experiment 24 provides an excellent method of preparation of methyl 3-oxo-1-cyclohexenyl phosphate (**15**). This γ-keto-α,β-



3

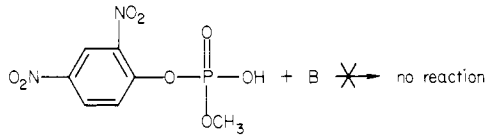


15

unsaturated phosphodiester is obtained in 90% yield when the methyl phosphonate monoanion (**3**) is allowed to decompose in the presence of 2 mol equiv of the β-diketone in dilute acetonitrile solution at 70 °C.

Consistent with the difficulty in generating monomeric methyl metaphosphate from the phosphonate methyl ester **3**, we find that

methyl 2,4-dinitrophenyl phosphate (**4**) is stable under comparable conditions.



4

Experimental Section

2,4-Dinitrophenyl dihydrogen phosphate (1) was prepared as described.[12]

Methyl 2,4-dinitrophenyl phosphate[13] **(4)** was isolated as its diisopropylethylammonium salt as follows. 2,4-Dinitrophenol was converted into dimethyl 2,4-dinitrophenyl phosphate (δ ^{31}P −6.4 ppm in $CDCl_3$) by reaction with dimethylphosphorochloridate in dichloromethane, in the presence of 1 mol equiv of imidazole. The phosphotriester was converted into methyl sodium 2,4-dinitrophenyl phosphate by reaction with sodium iodide in acetone. The sodium salt of **4** was dissolved in warm methanol, and the solution was passed through a column of Bio-Rad AG 50W-X-8 resin in the diisopropylethylammonium form. The column was eluted with methanol and the solution was evaporated at 20 °C (30 mm). The desired trialkylammonium salt (δ ^{31P} −7.6 ppm in CD_3CN) was freed from methanol by repeated evaporations with acetonitrile. Solutions of this salt in acetonitrile (0.4 M) were stable after 2 days at 25 °C and after 1 day at 70 °C.

***erythro*-1-Phenyl-1,2-dibromopropylphosphonic acid (2)** was prepared as shown in Scheme I, following the procedure of Kenyon and Westheimer.[7b] The acid **2** had mp 186–187 °C (after three recrystallizations from acetonitrile). **Dimethyl *erythro*-1-phenyl-1,2-dibromopropylphosphonate**[7c] **(19)** was obtained as an oil when a methanol solution of the acid **2** was treated with ethereal diazomethane. **Methyl *erythro*-1-phenyl-1,2-dibromopropylphosphonate**[7c] **(3)**, mp 158–159 °C (from acetonitrile) was obtained when an acetone solution of the triester **19** and LiBr was kept at 25 °C for 2 days, followed by acidification of an aqueous solution of the salt.

Decomposition of 2,4-Dinitrophenyl Dihydrogen Phosphate (1), *erythro*-1-Phenyl-1,2-dibromopropylphosphonic Acid (2), and Methyl Hydrogen *erythro*-1-Phenyl-1,2-dibromopropylphosphonate (3) in the Presence of a Tertiary Amine. Solutions of the phosphate and phosphonates in the solvents indicated in Table I were allowed to decompose in the presence of diisopropylethylamine, under the conditions indicated in the table. The course of the reactions was followed by ^{31}P and ^{1}H NMR spectrometry. The ^{31}P NMR spectra were obtained on a Brucker WH-360 spectrometer at 145.7 MHz. The ^{31}P chemical shifts of the pertinent compounds are summarized in Table II.

Methyl 3-Oxo-1-cyclohexenyl Phosphate (15). 1,3-Cyclohexanedione (0.024 g, 0.2 mmol; from Aldrich Chemical Co., stabilized with 3% NaCl) was mixed with CD_3CN (0.5 mL) and diisopropylethylamine (0.052 mL, 0.3 mmol). The clear solution was decanted into an NMR tube containing methyl *erythro*-1-phenyl-1,2-dibromopropylphosphonate (**3**; 0.037 g, 0.1 mmol). The ^{1}H NMR of the clear solution was observed at various times, at 25 and at 70 °C. After 17 h at 70 °C, the reaction was complete. The solution was evaporated at 35 °C (20 mm) and the residue was treated with diethyl ether (3 × 5 mL). The ether-soluble fraction contained 1-phenyl-1-bromopropene. The ether-insoluble fraction was the diisopropylethylammonium salt of methyl 3-oxo-1-cyclohexenyl phosphate; it was dissolved in water (5 mL) and was converted into the sodium salt by means of a Bio-Rad AG50W-X8 cation-exchange resin in its Na^+ form. Elution of the column with water (10 mL), and evaporation of the solution at 30 °C (20 mm) afforded **sodium methyl 3-oxo-1-cyclohexenyl phosphate** (0.028 g), δ ^{31}P −7.8 ppm; τ 4.10 ppm (vinyl proton) and 5.70 (methoxy protons); λ_{max} 254 nm (all measurements in D_2O).

The crude diisopropylethylammonium salt of methyl 3-oxo-1-cyclohexenylphosphate obtained by the above procedure was also purified by means of a column of DEAE-cellulose (Cellex-D), using a linear gradient of triethylammonium bicarbonate buffer. The triethylammonium salt of the enol phosphate methyl ester was converted into its sodium salt by NaI in methanol/acetone.

Monoanilinium 1-phenylethenyl hydrogen phosphate (12) was prepared from phenacyl chloride and trimethyl phosphite as described.[11] The anilinium salt (0.50 g) was dissolved in warm methanol (10 mL). The solution was passed rapidly through a column containing BioRad-AG 50W-X8 resin in its protonated form. The effluent was collected in a flask containing 1 mol equiv of diisopropylethylamine cooled to 0°, and the resulting solution was evaporated at 0 °C (0.5 mm). The residue was washed with ether and dried to yield **monodiisopropylethylammonium 1-phenylethenyl hydrogen phosphate**; δ ^{31}P −5.6 ppm (in CD_3CN). A 1 M CD_3CN solution of this salt containing 1 or 2 mol equiv of diisopropylethylamine exhibited no changes after 24 h at 25 °C.

Acknowledgment. The ^{31}P NMR measurements were carried out at Brookhaven National Laboratories under auspices of the U.S.A. Department of Energy. We are grateful to Dr. Alan McLaughlin and Mr. Donald Lawler for their assistance in obtaining NMR spectra.

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A ^{13}C and ^{29}Si NMR Spectroscopic Study of α- and β-Trimethylsilyl-Substituted Carbocations[1]

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Abstract: A series of trimethylsilyl-substituted carbocations was prepared under long-lived stable ion conditions at low temperatures and characterized by ^{13}C and ^{29}Si NMR spectroscopy. The α-trimethylsilyl group in the diphenyl(trimethylsilyl)methyl cation significantly deshields the cationic center in the ^{13}C NMR spectrum. At higher temperatures (≥0 °C) the diphenyl(trimethylsilyl)methyl cation undergoes rearrangement through methyl migration to the cationic center from the silicon atom followed by nucleophilic quenching of the developing silicon cation. No long-lived silicenium ion was, however, observed. Attempted generation of α-phenyl-α-(trimethylsilyl)ethyl and α-methyl-α-(trimethylsilyl)ethyl cations gave instead cumyl and *tert*-butyl cations through methyl migration, nucleophilic attack, oxidative β-desilylation, and subsequent protonation. (Trimethylsilyl)ethynyl-substituted carbocations besides showing the usual mesomeric vinyl cation character, also show significant β-carbon deshielding possibly due to C–Si pπ–dπ bonding. Protonated acyl silanes and their progenitors also show significant carbonyl carbon deshielding as compared to their carbon analogues.

The effect of silicon substituents on the reactivity and stability of organic compounds has been extensively studied in recent years.[2] Of particular interest is the effect of α- or β-silicon groups on an unsaturated organic moiety. The traditional view that a silyl

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