New Heterofunctional Cyclophosphazenes with Carbonyl and Double Bond Functions

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Enolate anions of ketones are ambident nucleophiles capable of interacting with electrophiles via C- or O-substitution pattern. Numerous attempts have been undertaken to elucidate the mechanism of their interaction with halogenophosphazenes.[1–4] Thus, the reactions of the lithium enolates of acetophenone,[1,3,4] cyclohexanone,[2a] and acetone[3,4] with hexachlorocyclophosphazene (1) were reported. In all cases the reactions were found to proceed exclusively via the "O" alkylation pathway. This led to the formation of the respective vinyloxy derivatives instead of the desired phosphazene compounds with a ketone function on the exocyclic group. The latter were of interest as possible precursors to a wide variety of new products of practical importance, which could be obtained via derivatization of carbonyl groups, capable of undergoing numerous addition and reduction type reactions.[5–7]

Whereas aldehyde groups have been succesfully introduced into cyclophosphazene via simple one-step substitution of 1 with hydroxybenzaldehyde,[8] and then derivatized,[8–13] ketone-substituted phosphazenes were found not to be available by direct synthetic routes. Some alternative indirect multistep methods toward their synthesis were developed, which led to more or less complicated reaction mixtures, giving low yields of the desired products.[4,8] Acetone-substituted phosphazene was isolated in 5% yield from the reaction of lithiophosphazene with α-bromoacetophenone; however, this reaction was found to be extremely complex and led to a variety of unidentified products.[4] A synthetic route to ketophosphazenes reported by Gallicano et al. required in its turn the use of relatively inaccesible, fully alkylated phosphazenes, $N_3P_3Me_6$ or $N_4P_4Me_8$, as starting materials.[8] Harris obtained acetonyl-substituted phosphazene by allowing the cupriophosphazene to react with 2-methoxyallyl bromide, followed by a subsequent hydrolysis step.[4]

(1) Du Pont, J. G.; Allen, C. W. *Inorg. Chem.* 1977, *16*, 2964.
(2) (a) Allen, C. W.; Ramachandran, K.; Bright, R. P.; Shaw, J. C. *Inorg. Chim. Acta* 1982, *64*, 109. (b) Ramachandran, K.; Allen, C. W. *Inorg. Chem.* 1983, 1445.
(3) Tate, D. P.; Hergenrother, W. G.; Kang, J. W.; Graves, F. *Polym. Prepr.* 1979, *20* (1), 177.
(4) Harris, R. J.; Schwalke, M. A. *Inorg. Chem.* 1983, *22*, 1812.
(5) Weininger & Stermitz, *Organic Chemistry*, Int. ed.; Academic Press Inc.: Orlando, FL 1984; pp 390–431.
(6) Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry;* W. A. Benjamin, Inc.: New York, 1964; Polish Edition; PWN: Warsaw 1969, pp 508–512.
(7) Kirk-Othmer, *Encyclopedia of Chemical Technology*, John Wiley & Sons Inc.: New York, London, Sydney, Australia, 1967; Vol. 12, pp 147–158.
(8) Gleria, M.; Lora, S.; Minto F.; Busulini, L.; Paolucci, G. *Chim. Ind. (Milan)* 1981, *63*, 719.
(9) Podda, G. *Gaz. Chim. Ital.* 1988, *118*, 397.
(10) Allcock, H. R.; Conolly, M. S.; Sisko, J. T.; Al-Shali, S. *Macromolecules* 1988, *21*, 323.
(11) Inoue, K.; Nitta, H.; Tanigaki, T. *Makromol. Chem., Rapid Commun.* 1990, *11*, 467.
(12) Chen-Yang Y. W.; Tsai, B. D.; Fan, S. *Phosphorus, Sulfur Silicon* 1990, Vol. 51/1–4.
(13) Fantin, G.; Medici, A.; Fogagnolo, M.; Pedrini, P.; Gleria, M.; Bertani, R.; Facchin, G. *Eur. Polym. J.* 1993, *29* (12), 1571.
(14) Gallicano, K. D.; Oakley, R. T.; Paddock, N. L.; Sharma, R. D. *Can. J. Chem.* 1981, *59*, 2654.
(15) Nakazawa, B. K. *J. Pharm. Soc., Jpn.* 1951, *71*, 85.
(16) Yaklakov, M. G.; Astrina, V. I.; Kireev, V. V. *Zh. Obshch. Khim.* 1986, *56*, 786.
(17) Yaklakov, M. G.; Astrina, V. I.; Kireev, V. V. *Zh. Obshch. Khim.* 1988, *58*, 2643.
(18) Allen, C. W. *Chem. Rev.* 1991, *91*, 119.

Looking for simpler and more efficient way of introducing ketone carbonyl function to cyclophosphazenes, we decided to study the reactions of readily available $N_3P_3Cl_6$ (1) with 1,3 diketones (β-diketones), like 2,4-dioxopentane (acetylacetone) and 1,3-dioxocyclohexane (1,3-cyclohexanedione). 1,3-Diketones are known to convert easily to enolate forms, RC(OH)=CHCOR′, tending to react as monobasic acids.[5–7,9] We have assumed some similarity of the designed reactions to the described previously reaction of 1 with acetoacetic acid—capable of keto–enolic tautomerism and easily converting into the respective sodium enolate. The latter was found to react with 1 by an O-phosphorylation pattern, yielding $N_3P_3Cl_{6-n}(OC(CH_3)=C(O)OEt)_n$ (n = 3, 6), in which the ester group remained untouched. As opposed to enolate anions, the sodium salts of diethymalonate and diethylmethylmalonate react with $N_3P_3Cl_6$ by attack at the carbon, not oxygen, site of the nucleophile (C-phosphorylation of malonate ester).[11]

To extend the knowledge about the reactions of various enolate anions with halophosphazenes this work was aimed at the elucidation of the direction of the substitution at the P atoms in phosphazene ring with the selected β-diketone potassium enolates (C- or O-reactive center?). Another target was to work up the simple efficient method of preparing phosphazene compounds with a ketone function at the exocyclic group by a direct one-step synthetic route.

Experimental Section

Materials. Hexachlorocyclotriphosphazene and potassium *tert*-butoxide were obtained from Aldrich and were used without further purification. Acetylacetone (Merck) was dried over anhydrous $MgSO_4$ and then distilled. 1,3-Cyclohexanedione (Aldrich) was dried by an azeotropic distillation of benzene. Tetrahydrofuran (POCh Gliwice) was distilled over CuCl, next over calcium hydride, and then twice over sodium–potassium alloy under an atmosphere of dry argon. *n*-Hexane (Merck) was used without purification. For column chromatography, silica gel 60 (230–400 mesh, Merck) was used. All reactions were performed under an atmosphere of dry argon.

Equipment. ^{1}H NMR spectra were recorded on a Varian VXR 300 spectrometer operating at 300 MHz using solutions in $CDCl_3$ with TMS as an internal reference. ^{31}P NMR spectra were recorded on the same spectrometer operating at 121 MHz using solutions in $CDCl_3$, and a solution of triphenylphosphate in $CDCl_3$ as an external reference. Mass spectra were recorded on a Finnigan Mat SSQ 700 spectrometer using the chemical ionization technique. IR spectra were performed with a Specord M80 spectrometer.

Preparation of Potassium Enolates of Acetylacetone and 1,3-Cyclohexanedione. Potassium *tert*-butoxide (0.02 mol,2.24g) was dissolved in 50 mL of THF, and a solution of diketone (0.02 mol) in 15 mL of THF was added dropwise over 20 min at room temperature. Reaction mixture was then stirring over 30 min. The obtained white suspension was used for further reactions directly after preparation.

Reaction of Potassium Enolates of Diketones with Hexachlorocyclotriphosphazene (1). The suspension of potassium enolate prepared as described above (0.02 mol) was added dropwise over 1 h at room temperature to a solution of hexachlorocyclotriphosphazene (0.025 mol, 8.7 g) in 50 mL of THF with vigorous stirring. After an additional 30 min of stirring, the precipitate of KCl was removed by centrifugation and THF was evaporated under vacuum. A sample (3 g) of brown residue was purified by column chromatography using 2:1 *n*-hexane/THF (compounds 2-4) or 15:1 (compounds 5-7) as eluents to obtain colorless liquids identified as the respective mono- (2 (yield 55%) or 5 (yield 50%)) and disubstituted derivatives (non-*gem* 3 (7%) or 6 (4%) and *gem* 4 (1%) or 7 (1%)). The mass and ^{1}H and ^{31}P NMR spectral data are presented in Tables 1 (compounds 2–4) and 2 (compounds 5–7). IR (cm^{-1}): compounds 2-4, 1630 (ν, C=O), 1560–1580 (ν, C=C), 1180–1220 (ν, P=N); compounds 5-7, 1710–1730 (ν, C=O), 1590–1640 (ν, C=C), 1180–1220 (ν, P=N).

Results and Discussion

The enolate anions used in this work were derived from acetylacetone and 1,3-cyclohexanedione, which are β-diketones

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Table 1. Structure and MS, ^{1}H NMR, and ^{31}P NMR Spectral Data for 1,3-Cyclohexanedione–Cyclotriphosphazene Derivatives

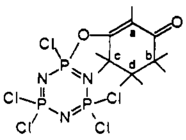
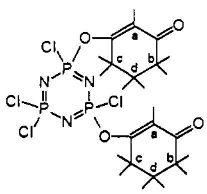
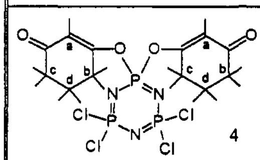
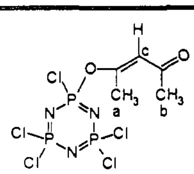
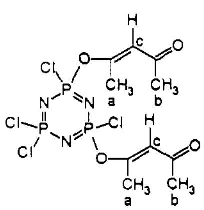
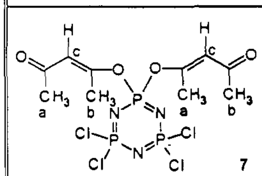
Compound	Formula MS (m/e)	^{31}P NMR				^{1}H NMR ν_H, ppm			
		ν_P, ppm			J_{P-P} Hz	H_a	H_b	H_c	H_d
		PCl_2	PCl(OR)	$P(OR)_2$					
 2	$C_6H_7O_2N_3P_3Cl_5$ 421 M^+ 326 M^+-C_6H_7O 310 M^+-$C_6H_7O_2$	23.01 dublet [2P]	10.14 triplet [1P]	–	63.75	6.01 singlet (1H)	2.59 triplet (2H) J_{H-H}= 14.8 Hz	2.38 triplet (2H) J_{H-H}= 13.4 Hz	2.09-2.01 multiplet (2H)
 3	$C_{12}H_{14}O_4N_3P_3Cl_4$ 497 M^+ 402 M^+-C_6H_7O 386 M^+-$C_6H_7O_2$	25.53 triplet [1P]	13.26 dublet [2P]	–	67.07	6.03 singlet (1H)	2.60 triplet (2H) J_{H-H}= 12.05 Hz	2.39 triplet (2H) J_{H-H}= 13.3 Hz	2.11-2.03 multiplet (2H)
 4	$C_{12}H_{14}O_4N_3P_3Cl_4$ 497 M^+ 402 M^+-C_6H_7O 386 M^+-$C_6H_7O_2$	25.08 dublet [2P]	–	-4.77 triplet [1P]	69.72	5.94 singlet (1H)	2.57 triplet (2H) J_{H-H}= 11.7 Hz	2.38 triplet (2H) J_{H-H}= 13.4 Hz	2.10-2.02 multiplet (2H)

Table 2. Structure and MS, ^{1}H NMR, and ^{31}P NMR Spectral data for Acetylacetone–Cyclotriphosphazene Derivatives

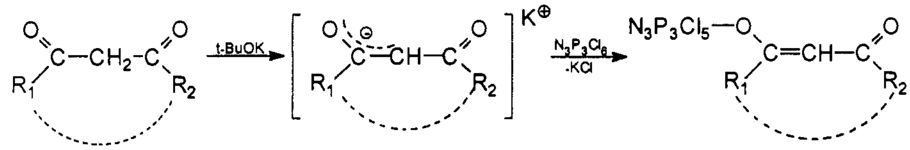
Compound	Formula MS (m/e)	^{31}P NMR				^{1}H NMR ν_H, ppm		
		ν_P, ppm			J_{P-P} Hz	H_a	H_b	H_c
		PCl_2	PCl(OR)	$P(OR)_2$				
 5	$C_5H_7O_2N_3P_3Cl_5$ 409 M^+ 326 M^+-C_5H_7O 310 M^+-$C_5H_7O_2$	23.05 dublet [2P]	10.54 triplet [1P]	–	62.44	2.43 singlet (3H)	2.27 singlet (3H)	6.28 singlet (1H)
 6	$C_{10}H_{14}O_4N_3P_3Cl_4$ 473 M^+ 390 M^+-C_5H_7O 374 M^+-$C_5H_7O_2$	25.33 triplet [1P]	13.55 dublet [2P]	–	66.34	2.45 singlet (3H)	2.29 singlet (3H)	6.29 singlet (1H)
 7	$C_{10}H_{14}O_4N_3P_3Cl_4$ 473 M^+ 390 M^+-C_5H_7O 374 M^+-$C_5H_7O_2$	24.65 dublet [2P]	–	-5.02 triplet [1P]	64.33	2.46 singlet (3H)	2.30 singlet (3H)	6.32 singlet (1H)

containing two carbonyl functions separated by one methylene group. In carbon chemistry both "O" and "C" substitution routes are observed to compete in the reactions of ketone enolates with alkyl halides.[5–7] However only "O"-phosphorylation pattern has been hitherto reported for the reactions of various keto–enolates with halophosphazenes. In the case of the previously employed monoketones such a mechanism yielded exclusively the respective vinyloxy derivatives with an olefinic double bond as a function.[1–3,10] However, considering the known tendency of 1,3-diketones to react as monobasic acids[5–7] one could expect that their respective reactions with hexachlorocyclotriphosphazatriene (**1**) would proceed with the involvement of only one carbonyl function, thus leading to the heterofunctional derivatives (**2, 5**) containing both double bond and carbonyl group as the functions, according to Scheme 1.

Reactions of enolate anions of acetylacetone and 1,3-cyclohexanedione with hexachlorocyclotriphosphazatriene (**1**) were carried out at a 1:1 molar ratio of reagents, aiming at the preparation of the respective monosubstituted cyclophosphazene derivatives **2** and **5**. The course of the reaction was monitored by the TLC technique, the reaction being considered to be completed at full conversion of the enolate. The reaction mixtures obtained were separated by means of flash chromatography on silica gel.

Mass and NMR (^{1}H and ^{31}P) spectral data of the respective chromatographically isolated pure compounds (Tables 1 and 2)

Scheme 1



2: –R_1—R_2– =–CH_2-CH_2-CH_2–
5: R_1=R_2=CH_3

have confirmed the assumed reaction pattern (Scheme 1) involving O-phosphorylation at the enolized end of the diketone monoenolate with the introduction of the second carbonyl function untouched into the derivatized cyclophosphazene molecule. The favourable combination of the hard acid (phosphorus(V)) with the hard base (oxygen) resulted in an exclusive attack at the oxygen atom of the enolate anion, similarly as in the reactions of **1** with monoketones described by Allen et al.[1,2]

Both reactions were found to yield the respective monooxy-[oxo(alkyl (**2**) or cycloalkyl (**5**))ene]-substituted derivatives, respectively, as the major products (~50% of the theoretical yield). Small amounts of the corresponding isomeric *gem* (**3, 6**) and non-*gem* (**4, 7**) disubstituted derivatives have also been isolated, the respective non-*gem* isomers being always formed preferably (see Experimental Section). Non-geminal regioselectivity is typical for substitution reactions of halogenophosphazenes with oxyanions.[12]

^{31}P NMR spectra of all the obtained derivatives represent spin systems of A_2B type, with the chemical shifts ν_P, coupling constants J_{P-P} and the respective intensity ratios [A]/[B] consistent with the assumed structures (**2–7**). The ^{1}H NMR spectra revealed all the protons characteristic for the proposed structures, their intensities corresponding to the relative ratios of the protons a-c (**2–4**) or a-d (**5–7**) in the respective formulas (Tables 1 and 2).

Mass spectra have shown molecular ions consistent with the respective molecular masses (**2–7**), accompanied by the fragmentation peaks resulting from the loss of the corresponding substituent, originating from the respective diketone. The linking oxygen atom were either split off together with the respective organic residue or left on the cyclophoshazene fragment—both fragmentation routes being observed (Tables 1 and 2).

IR spectra confirm the retention of a cyclophosphazene skeleton and the presence of C=O and C=C bonds in all of synthesized compounds (Experimental Section).

Due to the selective involvement of only one carbonyl group in the each diketone molecule into the interaction with **1** this reaction provides a direct route to hitherto inaccessible α,β-unsaturated ketone-containing cyclophosphazene derivatives, which can serve as heterofunctional starting materials to various types of addition and polyaddition reactions.

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