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A REINVESTIGATION OF THE REACTIONS OF ENOLATE ANIONS WITH CYCLOTRIPHOSPHAZENES

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Abstract

The reactions of enolate anions with hexahalocyclotriphosphazenes have been reexamined. Based on N.M.R. spectroscopic data, structures of the type $N_3P_3X_5OCR{=}CH_2$ (X=F,Cl; R=H,C_6H_5) are proposed.

Introduction

Enolate anions of ketones are ambident nucleophiles which have attracted considerable attention (1). We have previously reported the reactions of the lithium enolate anions of acetophenone and cyclohexanone with hexafluorocyclotriphosphazene, $N_3P_3F_6$, and based on limited nmr data suggested that attack occurred at the carbon end of the nucleophile leading to ketones with the phosphazene moiety bonded to the α-carbon atom (2). Recently, Tate et.al. reported the reactions of polydichlorophosphazene with various enolate anions and proposed that attack occurred at the oxygen end of the nucleophile (3), thus leading to vinyl alcohol derivatives. This investigation is an attempt to resolve these conflicting interpretation concerning the nature of these materials.

Experimental

Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, (Ethyl Corp.) was recrystallized from petroleum ether to a constant m.p. 113°C n-Butyl lithium (1.6M solution in hexane) was obtained from Aldrich. Tetrahydrofuran (THF)(Aldrich) was distilled from sodium-benzophenone ketyl. Petroleum ether (b.p. 35-55°C), benzene and ethyl acetate (Fisher) were distilled by standard procedures. NMR spectra (in $CDCl_3$) were recorded on a Bruker WM250 spectrometer operating at 250.1 MHz (^1H), 62.9 MHz (^{13}C), and 101.2 MHz (^{31}P). Tetramethyl silane (TMS) was used as an internal reference for ^1H and ^{13}C NMR measurements. For ^{31}P NMR, 85% H_3PO_4 was used as an external standard. Chemical shifts upfield to the reference are assigned a negative sign. ^{13}C and ^{31}P NMR spectra were recorded under conditions of broad band decoupling. Infrared (IR) spectra were obtained as their thin films (NaCl discs) on a Beckman IR 20A spectrometer. Mass spectra were recorded on a Perkin-Elmer RMU-6D spectrometer operating at 80 eV. Elemental analyses were performed by Integral Microanalytical Laboratories. Hexafluorocyclotriphosphazene (4) and the derivatives derived from the enolate anions of acetophenone (I, $N_3P_3F_5OC_8H_7$) and cyclohexanone (II, $N_3P_3F_5OC_6H_9O$) (2) were prepared by previously reported procedures.

Preparation of $N_3P_3Cl_5OCH{=}CH_2$ (III). A solution of n-butyl lithium (45 mL, 0.07 mol) was added to tetrahydrofuran (THF)(75 mL) at room temperature, using the apparatus described elsewhere (5). The resulting reaction mixture was stirred for 16 hr then slowly added to a solution of 10.5 g (.03 mol) of $N_3P_3Cl_6$ in tetrahydrofuran at 0°C under a nitrogen atmosphere. The resulting mixture was allowed to come to room temperature and was kept stirred for four days. The solvent was removed and the residue extracted with hexane. Following filtration and removal of hexane, 10.2 g of a pale yellow liquid was obtained. A 2 gm sample of this material was purified using the flash chromatography technique (6) using petroleum ether as the eluant. A 0.92 g (44.3% of theory) sample of a colorless liquid, b.p. 75° at 0.05 mm Hg was obtained. Anal. Calcd. for $N_3P_3Cl_5OC_2H_3$ (III): C, 6.75; H, 0.84; mol wt 353. Found: C, 6.74; H, 0.75; mol wt 353 (mass spectrum).

IR(cm^{-1}): 1650(s, C=C str), 1220(s, PN str), 1110(s, PO str), 1035(s), 930(w, PCl), 875(m, PCl) 750(m, PCl).

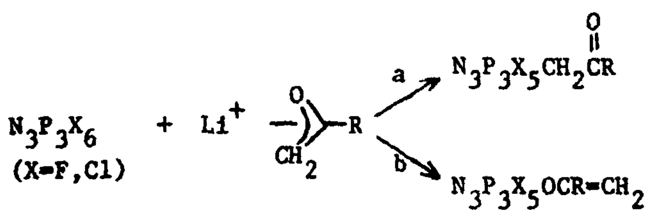
Preparation of $N_3P_3F_5OCH{=}CH_2$ (IV). The reaction of 40 mL (0.064) of n-butyl lithium solution in excess THF was added to 16.0 g (0.064 mol) of $N_3P_3F_6$ as previously described. After removal of most of the solvent, the remaining product/solvent mixture was carefully fractionated at room temperature. The remaining solvent distilling at 5 mm Hg and the product at 1 mm Hg. A sample of 0.56 g (3.2% of theory) of a colorless liquid was obtained. Anal. Calcd. for $N_3P_3F_5OC_2H_3$ (IV): mol wt 273. Found: mol wt 273 (mass spectrum).

IR(cm^{-1}): 1645(m, C=C), 1290(s, PN str), 1125(s, PO str), 1060(m), 1010(m), 950(s, PF asym), 880(s), 845(s, PF), 800(m).

Attempted Derivatization of I and II. In separate experiments, the acetophenone (I) and cyclohexanone (II) derivatives of $N_3P_3F_6$ were treated with bromine (Br_2/CCl_4) and hydrogen (H_2/10% Pt on activated carbon). In both the bromination and hydrogenation experiments, a large number of products formed which resisted separation.

Results and Discussion

The two possible reaction pathways for the ambident enolate anions with a hexahalocyclotriphosphazene are shown below. Our first attempt at resolving this question involved derivatiza-



tion with bromine on hydrogen. If the vinyloxy (route b) derivative formed, then the simple addition compounds would be readily identifiable. Unfortunately, these reactions gave rise to a large number of products so we turned our attention to nmr spectroscopic techniques. In order to gain more useful information from the nmr studies, we prepared derivatives containing hydrogen

TABLE

Selected N.M.R. Data[a]

Compound			$^{13}C^{b}$	$^{31}P^{c}$
$\equiv P(F)OC_1(C_6H_5)=C_2H_6H_a$	(I)	$\delta H_a = 5.19$; (COMPLEX MULTIPLET)	$\delta C_1 = 152.43$, $^2J_{PC} = 7.94$	$\delta \equiv PFR = 14.84$, $^1J_{PF} = 907.43$
		$\delta H_b = 5.43$; (COMPLEX MULTIPLET)	$\delta C_2 = 100.11$, $^3J_{PC} = 5.28$	$\delta \equiv PF_2 = 10.02$, $^1J_{PF} = 937.55$
$\equiv P(F)OC_1=C_2H_a$ (C1–C2 bridged by –$(CH_2)_4$–)	(II)	$\delta H_a = 5.58$; (COMPLEX MULTIPLET)	$\delta C_1 = 147.95$, $^2J_{PC} = 9.24$	$\delta \equiv PFR = 15.52$, $^1J_{PF} = 919.01$
			$\delta C_2 = 114.49$, $^3J_{PC} = 6.40$	$\delta \equiv PF_2 = 10.30$, $^1J_{PF} = 932.13$
$\equiv P(Cl)OC_1(H_x)=C_2(H_b)-H_a$	(III)	$\delta H_x = 6.55$; $^3J_{H_xH_a} = 13.43$, $^3J_{H_xP} = 7.63$	$\delta C_1 = 140.21$, $^2J_{PC} = 7.40$	$\delta \equiv PClR = 13.24$, $^2J_{PP} = 64.70$
		$^3J_{H_xH_b} = 5.80$		
		$\delta H_a = 5.16$; $^3J_{H_aH_x} = 13.43$, $^4J_{H_aP} = 2.75$	$\delta C_2 = 104.27$, $^3J_{PC} = 14.80$	$\delta \equiv PCl_2 = 23.36$, $^2J_{PP} = 63.48$
		$^2J_{H_aH_b} = 2.44$		
		$\delta H_b = 4.89$; $^3J_{H_bH_x} = 5.80$, $^4J_{H_6P} = 2.59$		
		$^2J_{H_bH_a} = 2.44$		
$\equiv P(F)OC_1(H_x)=C_2(H_b)-H_a$	(IV)	$\delta H_x = 6.48$; $^3J_{H_xH_a} = 13.43$, $^3J_{H_xP} = 7.02$	$\delta C_1 = 140.29$, $^2J_{PC} = 6.27$	$\delta \equiv PFR = 11.18$, $^1J_{PF} = 887.67$
		$^3J_{H_xH_b} = 5.80$		
		$\delta H_a = 5.13$; $^3J_{H_aH_x} = 13.43$, $^4J_{H_aP} = 2.44$	$\delta C_2 = 104.31$, $^3J_{PC} = 10.99$	$\delta \equiv PF_a = 10.97$, $^1J_{PP} = 909.97$
		$^2J_{H_aH_b} = 2.44$, $^5J_{H_aF} = 0.61$		
		$\delta H_b = 4.85$; $^3J_{H_bH_x} = 5.80$, $^4J_{H_bP} = 2.75$		
		$^2J_{H_bH_a} = 2.44$, $^5J_{H_bF} = 1.22$		

a. All coupling constants are given in Hz
b. ^1H and ^{13}C chemical shifts are given in ppm relative to TMS
c. ^{31}P chemical shifts are given in ppm relative to 85% H_3PO_4

atoms on both carbon atoms. The enolate anion of acetaldehyde is quantitatively generated from the metalation of THF with n-butyl lithium (7).

$$C_4H_8O + n\text{-}C_4H_9Li \longrightarrow LiOC_2H_3 + C_2H_4 + C_4H_{10}$$

and gives derivatives of both the hexachloro- and hexafluorocyclotriphosphazene. The nmr data

$$LiOC_2H_3 + N_3P_3X_6 \longrightarrow N_3P_3X_5OC_2H_3 \qquad \begin{matrix} \text{III: X=Cl} \\ \text{IV: X=F} \end{matrix}$$

(^1H, ^{13}C, ^{31}P) for compounds I-IV are reported in the table.

The ^1H nmr spectrum of III closely resembles that of vinyl acetate except for the additional phosphorus coupling for each proton and can be analyzed as such. The observed spectrum is not consistent with a carbon bonded derivative since H_x exhibits more extensive coupling than it would as an aldehyde proton. The chemical shifts are more appropriate for olefinic rather than for alkyl and aldehyde protons. The same arguments apply to IV. The previous ^1H nmr data on compounds I and II were obtained at 60 MHz and were poorly resolved (2). In the 250 MHz spectrum, the additional coupling appropriate to an olefin but not to an α-substituted ketone, is observed. The separation between H_a and H_b in I is too large to be ascribed to $J_{P_{CH}}$ in an alkylphosphazene (8). Furthermore, only H_a is observed in II, thus the two peaks (H_a, H_b) observed in I are not reasonably ascribed to phosphorus-proton coupling. The strongest evidence favoring the bonding of the enol form comes from the ^{13}C nmr data. There are no resonances in the alkyl or carbonyl ranges (9) while those in the olefin range match the number predicted from a vinyloxy derivative. The assignments of C_1 and C_2 shifts in III were confirmed by off resonance decoupling in which C_1 becomes a doublet and C_2 a triplet. The large shielding of C_1 is due to mesomeric interactions of C_1 with oxygen lone pair electrons (9). The magnitude of the phosphorus-carbon coupling constants is variable and doesn't provide a useful structural tool in this case. The ^{31}P nmr spectra of I-IV show little variation with or without broad band proton decoupling. If the phosphorus atom were bonded to a methylene group, significant $J_{P_{CH}}$ effects would be observed in the ≡PXR resonance.

All of the nmr data which we have presented support the proposal of Tate (3) that attack of the enolate is at the oxygen end, rather than at the carbon end, of the nucleophile. The IR data are also consistent with this conclusion. The bands around 1650 cm^{-1} can be ascribed to olefinic stretching modes rather than carbonyl modes and bands around 1130 cm^{-1} can be assigned to a POC vibration rather than unusual PN vibrations. These materials, especially the newly reported III and IV, represent another example of organofunctional phosphazenes (10) which may be expected to exhibit interesting monomer and polymer chemistry. Work along these lines is currently in progress in our laboratory.

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