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Kinetic Isotope Effects on Metaphosphate Generation from Fragmentation of 2,3-Oxaphosphabicyclo[2.2.2]octene Derivatives

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ABSTRACT

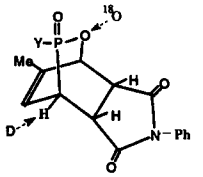
*Kinetic isotope effects of deuterium and oxygen-18 were measured on fragmentation of syn-3-ethoxy (***1a***) and syn-3-(N,N-diethylamino) (***1b***) 2,3-oxaphosphabicyclo[2.2.2]octene derivatives in 1,2-dichloroethane at 100°C. The secondary deuterium isotope effect on hydrogen adjacent to the P–C bond was found to be 1.060 ± 0.008 for* **1a** *and 1.081 ± 0.009 for* **1b**. *The kinetic oxygen isotope effect on the bridge P–O–C is 0.9901 ± 0.0016 for* **1a**. *The data indicate an unsymmetrical transition state for retrocycloaddition extrusion of the metaphosphate moiety, with the breakage of the C–P bond and formation of the P = O bond more advanced than the C–O breakage. A synthesis of* **1a** *and* **1b** *labeled with deuterium is described. © 1996 John Wiley & Sons, Inc.*

INTRODUCTION

From our earlier kinetic studies of fragmentation of the 2,3-oxaphosphabicyclo[2.2.2]octene system type **1**, we concluded that formation of metaphosphoric acid derivatives **3** occurred by a retrocycloaddition mechanism (Scheme 1) [1]:

Metaphosphates are highly electrophilic in solution [2] and undergo immediate intermolecular condensation to form P–O–P derivatives [1]. When alcohol is added, the corresponding phosphate (**4a**) or phosphoramidate (**4b**) is formed. Phosphoramidates are not stable and react further with replacement of the amino group to form phosphates $(RO)_2POOH$ [3,4].

The extrusion of **3** requires cleavage of both the C–P and C–O bonds. To probe the structure of the transition state leading to metaphosphate, we have now measured the effect of isotopic substitution at two positions. The hydrogen on C of the P–C unit was replaced by deuterium, oxygen in the P–O–C bridge was labeled with oxygen-18.



The magnitude of the secondary deuterium isotope effect (KIE) primarily is related to changes in the out-of-plane bending vibrations [5]. Because the hydrogen atom was substituted for deuterium at the carbon atom, which changes its hybridization from sp^3 to sp^2 along the reaction path, the normal KIE ($k_H/k_D > 1$) is expected.

The value of oxygen-18 KIE will reflect the changes of bonding at the bridge oxygen atom. The oxygen isotope effect k_{16}/k_{18} should be larger than

Dedicated to Professor Louis D. Quin on the occasion of his retirement from the University of Massachusetts at Amherst.

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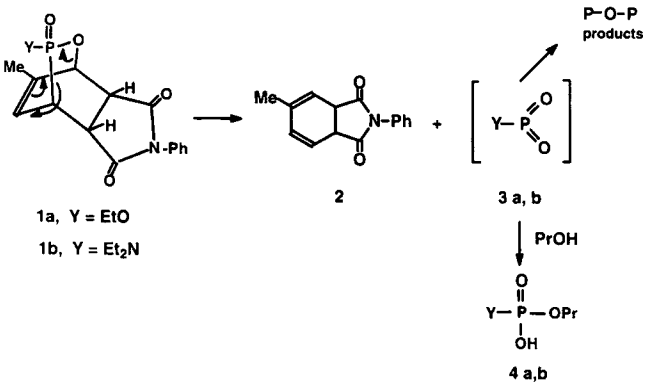


SCHEME 1

unity for the C–O bond breakage. A smaller or even inverse isotope effect ($k_{16}/k_{18} < 1$) will reflect the degree of double-bond character of the forming P–O bond and hence the positive charge of the bridge atom [6].

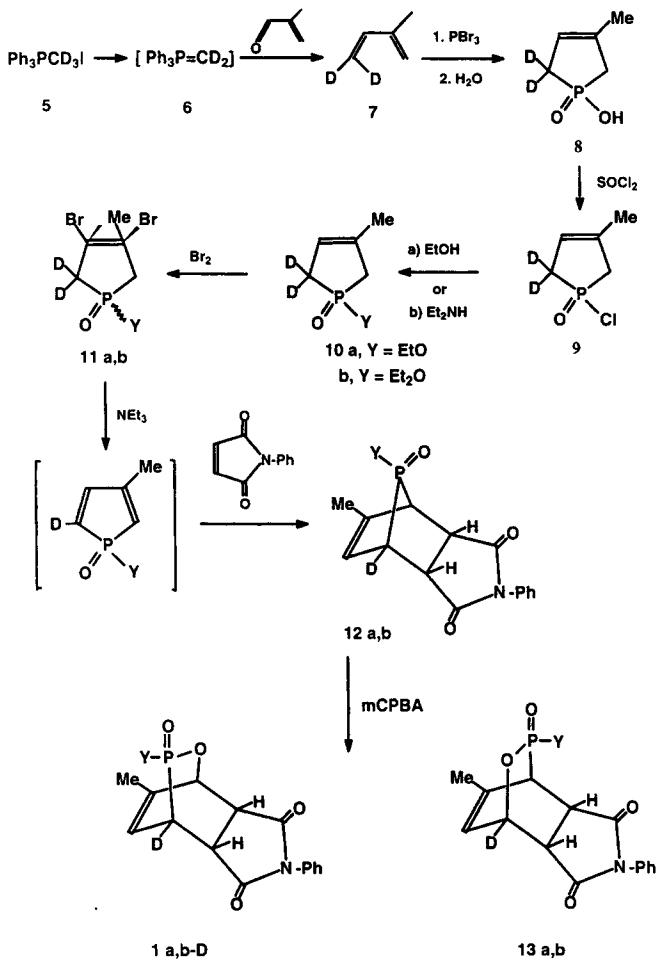
RESULTS AND DISCUSSION

Synthesis of Labeled Substrates

To replace the hydrogen with deuterium on a carbon of the P–C unit, we performed a multistep synthesis by adaptation of known methods [3,7–10] (Scheme 2). 4,4-Dideuterio-2-methyl-1,3-butadiene (**7**) was prepared by the Wittig reaction of methacrolein with ylide $Ph_3P{=}CD_2$ (**6**), readily synthesized from (methyl-d_3)triphenylphosphonium iodide (**5**) in a solution of DMSO-d_6. Isoprene-d_2 (**7**) was directly used in synthesis of 5,5-dideuterio-1-hydroxy-3-methyl-3-phospholene-1-oxide (**8**), which was converted into a chloride (**9**), and then 1-ethoxy (**10a**) and N,N-diethylamino (**10b**) derivatives were obtained. Subsequent bromination of **10a** and **10b**, followed by addition of N-phenylmaleimide in the presence of triethylamine, gave the Diels-Alder adducts **12a** and **12b**. The adducts **12a** and **12b** were oxidized by m-chloroperbenzoic acid to afford the mixtures of isomers **1a-D** and **13a**, and **1b-D** and **13b**. The pure products **1a-D** and **1b-D** were isolated by recrystallization, and the overall yield was 3.1% (**1a-D**) and 1.8% (**1b-D**) with respect to isoprene-d_2 (**7**) (the yield of **1a-D** was higher due to addition of unlabeled **1a** during the final recrystallization).

Scheme 2: Synthetic Route to **1a-D** *and* **1b-D** *Labeled with Deuterium*

To incorporate the oxygen-18 into **1a** or **1b**, we treated the corresponding Diels-Alder adducts with m-chloroperbenzoic acid labeled with oxygen-18, as



SCHEME 2

described elsewhere [11], with a yield of 36% with respect to the phosphorus substrate.

Kinetic Isotope Effects

The fragmentation of **1a** and **1b** in the presence of 1-propanol in 1,2-dichloroethane at 100°C follows first-order kinetics with the rate constants of $(8.50 \pm 0.20) \cdot 10^{-5}$ s^{-1} and $(9.38 \pm 0.24) \cdot 10^{-5}$ s^{-1}, respectively. These values are in good agreement with previously reported rates of decomposition of **1a** and **1b** in other solvents [1], as was expected due to a small solvent effect. The values of the kinetic isotope effects are given in Table 1.

The secondary deuterium isotope effects on fragmentation of **1a** and **1b** are 1.060 ± 0.008 and 1.081 ± 0.009, respectively. For reactions in which a carbon atom changes its hybridization from sp^3 to sp^2, the secondary deuterium KIE is expected to be 1.4 if the transition state is very close to the sp^2 product. For S_N1-type reactions, the isotope effect is typically around 1.15–1.25 [12]. However, for retro-Diels-Al-

TABLE 1 Kinetic Isotope Effects on Fragmentation of **1a** and **1b**

Compound	*f*[a]	$R^b = I_{350}/I_{348}$	$R^b = I_{241}/I_{240}$	k_{16}/k_{18}	k_H/k_D
1a-^{18}O	0.2	0.40068 ± 0.00059		0.9901 ± 0.0016[d]	
	0.3	0.40040 ± 0.00088			
	0.4	0.39984 ± 0.00075			
	0.5	0.39883 ± 0.00088			
	1.0	0.39575 ± 0.00036[c]			
1a-D	0.2		0.7713 ± 0.0040		1.060 ± 0.008[d]
	0.3		0.7727 ± 0.0041		
			0.7734 ± 0.0032		
	0.36		0.7759 ± 0.0038		
	0.5		0.7906 ± 0.0028		
	1.0		0.8286 ± 0.0029		
1b-D	0.2		0.7486 ± 0.0040		1.081 ± 0.009[d]
	0.3		0.7504 ± 0.0041		
	0.4		0.7641 ± 0.0038		
	0.5		0.7738 ± 0.0028		
	1.0		0.8237 ± 0.0029		

[a]Value calculated from the rate constant.
[b]Value corrected for natural isotopic composition.
[c]The average value from five measurements.
[d]The error reported is the standard deviation.

der reactions, this effect is smaller and close to 1.08 [13]. From recent theoretical calculations, it was concluded [14] that this magnitude of effect corresponds to a concerted mechanism. The calculated value of KIE for the stepwise mechanism is about 10% larger.

Diethylamine derivative **1b** fragments faster [1] and has a larger KIE, which corresponds to more advanced carbon–phosphorus bond breakage, reflecting a more "productlike" transition state. The magnitude of deuterium effects allowed the exclusion of a stepwise mechanism with a transition state leading to an ionic intermediate with only the C–P bond broken, and supports our previous conclusion [1] drawn from the small solvent effect.

For further exploration of the transition state, we considered different experimental approaches. One was to measure the secondary deuterium effect at the carbon adjacent to oxygen. A second one was to label substrates simultaneously at two positions and determine if effects at one and two positions are multiplicative or not [15]. Another possibility was to measure the oxygen-18 effect on the P–O–C bridge. We chose the last method because **1a** and **1b** labeled with oxygen-18 are available in a shorter synthetic path [11].

The use of heavy atom KIE in the study of the Diels-Alder reaction is limited to only two cases [16,17]. To our knowledge, the oxygen isotope effect was applied only to study the mechanism of the decarboxylation of the maleic anhydride adduct of α-pyrone [18]. Isotope effects of oxygen and carbon were determined by mass spectral analyses of carbon dioxide at the level of natural abundance, giving $k_{16/18} = 1.015 \pm 0.002$ and $k_{12/13} = 1.032 \pm 0.001$, respectively. From theoretical data analysis [19], it was concluded that, in the transition state, the carbon–carbon bond is effectively broken, the carbonyl bond is tightened, and the carbon–oxygen bond remains virtually intact.

The oxygen isotope effect was measured only for **1a** (Table 1). The product of fragmentation of **1b**, phosphoramidate $(Et_2N)(PrO)POOH$ decomposes [4] during the reaction and cannot be used for determination of the isotope effect. Attempts to determine the oxygen effect from isotopic analysis of **1b** were unsuccessful due to the fragmentation of the molecular ion during the mass spectrometric measurements. Details of this fragmentation are described elsewhere [20].

The inverse value of the oxygen isotope effect $k_{16}/k_{18} = 0.9901 \pm 0.0016$ on fragmentation of **1a** reflects a transition state with an increase of bonding around the bridge oxygen. The formation of an additional bond to the oxygen atom ($=O^{\oplus}-$) was proposed to explain the inverse oxygen KIE on acid-catalyzed hydrolyses of glucopyranosides (α-methyl, 0.996; β-methyl, 0.991) [21] and 2-propyl α-arabinofuranoside (0.988) [22].

A large inverse KIE of 0.984 for the oxygen atom linked to phosphorus was found in the enzymatic hydrolysis of 3,3-dimethylbutyl p-nitrophenyl phos-

phate and was concluded to be a result of activation of the phosphoryl oxygen by its protonation in the transition state [23]. We considered also the possibility of protonation of substrate **1** by alcohol or product **4**:

$$ROH + O{=}P\text{-}O\text{-}C \rightleftharpoons RO\cdots H\cdots O^{\delta-}\cdots P^{\delta+}\cdots O\text{—}C \quad (1)$$

which may also lead to the inverse oxygen effect. However, the kinetic measurements [1] do not support this pre-equilibrium concept. The rate of fragmentation of **1** is independent of the alcohol concentration and does not accelerate during the reaction, as would be expected if the product were involved in equilibrium (1).

CONCLUSIONS

From both the deuterium and oxygen kinetic isotope effects, we can propose the asynchronous retrocycloaddition mechanism for fragmentation of the 2,3-oxaphosphabicyclo[2.2.2]octene ring system. The breakage of the C–P bond and formation of the P=O bond precedes the C–O bond breakage in the transition state that leads to the extrusion of metaphosphate **3**. These new results are additional proof for formation of metaphosphate as a discrete intermediate, as was proposed previously from kinetic studies [1].

EXPERIMENTAL

General

^1H and ^{31}P spectra were recorded on an IBM NR-80 spectrometer at 80 and 32.38 MHz, respectively, in $CDCl_3$ solutions. Melting points are uncorrected. 1,2-Dichloroethane was distilled twice from P_2O_5 shortly before use. Methacrolein (Aldrich) was distilled directly before use. DMSO-d_6 (Polatom, Poland), iodomethane-d_3 (99.8%, VEB Berlin Chemie, Germany), and other solvents and reagents used for synthesis were purified using standard procedures.

Synthesis of Substrates

Unlabeled *syn*-3-ethoxy-6-methyl-N-phenyl-2,3-oxaphosphabicyclo[2.2.2]oct-5-ene-8,9-dicarboximide 3-oxide (**1a**) and *syn*-3-(N,N-diethylamino)-6-methyl-N-phenyl-2,3-oxaphosphabicyclo[2.2.2]oct-5-ene-8,9-dicarboximide 3-oxide (**1b**) were prepared and purified as reported previously [3,7]. The synthesis of **1a**-^{18}O has been published earlier [11] and gave a product containing 30.8% ^{18}O from fast atom bombardment mass spectrometry (FABMS). The same method was used for preparation of **1b**-^{18}O.

(Methyl-d_3)triphenylphosphonium Iodide (**5**) *[8,9].* Iodomethane-d_3 (19.4 g, 0.134 mol) was added dropwise with stirring under a nitrogen blanket to a solution of triphenylphosphine (23.5 g, 0.09 mol) in 50 mL of benzene. The reaction is exothermic; the solution warmed to boiling and then was left at room temperature for 15 hours. The precipitated solid was washed with benzene and dried under a vacuum over P_2O_5. Yield 27.9 g (75.0%).

4,4-Dideuterio-2-methyl-1,3-butadiene (**7**). Isoprene-d_2 (**7**) was synthesized according to a known procedure [9] but with some modifications. Sodium hydride (0.467 g (80%), 15.6 mmol) was placed in a 100-mL three-neck flask and washed with dry pentane. The solvent was removed by evaporation; the flask was flushed with dry nitrogen, and 7.5 mL of dry DMSO-d_6 (about 90% D) was added. The suspension was stirred vigorously at 55°C to completion of the evolution of gas (about 90 minutes). The solution was cooled with a room-temperature water bath, and a solution of 6.2 g (15 mmol) of (methyl-d_3)triphenylphosphonium iodide (**5**) in 15 mL of DMSO-d_6 was added dropwise and left for an additional 20 minutes. The flask was attached to a trap placed in a liquid nitrogen bath, and 1.5 mL of methacrolein (1.28 g, 18 mmol) was added using a syringe. The reaction mixture was stirred for 1 hour at room temperature and then for 1.5 hours at 60°C. The yield of **7** collected in the trap was 0.71 g (10.2 mmol, 68%). The product was used directly in the next step.

5,5-Dideuterio-1-hydroxy-3-methyl-3-phospholene-1-oxide (**8**). The synthesis of **7** was carried out by a known method [10]. Phosphorus tribromide (2.7 g, 10.5 mmol) and 50 mg of copper stearate were added to a solution of (**7**) (0.71 g, 10.2 mmol) in 10 mL of dry pentane. The reaction mixture was sealed in a flask under nitrogen and was left at room temperature. After a few days, the solid cycloadduct started to precipitate, and in four weeks, the reaction mixture solidified completely. It was transferred to a beaker containing sodium bicarbonate (3.36 g, 40 mmol) and 10 mL of cold water and then placed in an ice bath. When vigorous evolution of CO_2 had been completed, the precipitated NaBr was collected by filtration. The solution was washed four times with 10 mL of chloroform and then acidified with hydrochloric acid. The product was extracted with chloroform, and the solvent was removed by rotary evaporation to give 0.82 g (6.0 mmol, 60.0%) of **8** as a yellow viscous oil. ^{31}P NMR: δ 72.0; ^1H NMR: δ 1.80 (s, 3H), 2.41 (d, 2 H, $^2J_{PH}$ = 12.8 Hz), 5.51 (d, 1 H, $^2J_{PH}$ = 3.6 Hz), 8.70 (s, 1 H).

1-Chloro-5,5-dideuterio-3-methyl-3-phospholene-

1-oxide (**9**). The acid (**8**) was dissolved in 10 mL of chloroform, and thionyl chloride (0.90 g, 7.5 mmol) was added. After 15 minutes of stirring, the reaction was found by ^{31}P NMR spectroscopy to be complete after 15 minutes. Concentration by rotoevaporation and then high vacuum gave **9** (^{31}P NMR: δ 83.7) as a light brown oil (0.93 g, 100%), which was used directly in the next step.

Synthesis of the 2,3-oxaphosphabicyclo[2.2.2]octene-3-oxides **1a-D** *and* **1b-D**. The synthesis was performed in four steps by adaptation of known methods [3,7].

Step 1. The crude 1-chlorophospholene 1-oxide (**9**) (0.93 g, 7.5 mmol) was dissolved in 10 mL of dry benzene, and the solution was divided in two equal parts. To one part, ethanol (0.161 g, 3.5 mmol) and triethylamine (0.354 g, 3.5 mmol) were added, and diethylamine (0.512 g, 7 mmol) was added to the second solution. The reaction mixtures were stirred at room temperature for 20 hours. In each case, the amine hydrochlorides were removed by filtration, and benzene was removed from the filtrates. 5,5-Dideuterio-1-ethoxy-3-methyl-3-phospholene-1-oxide (**10a**) exhibited a ^{31}P NMR resonance at δ 71.6; 5,5-dideuterio-1-N,N-diethylamino-3-methyl-3-phospholene-1-oxide (**10b**) had ^{31}P NMR δ 65,4.

Step 2. Five milliliters of chloroform was added to prepare solutions of **10a** and **10b**, to which portions of bromine (0.48 g, 3 mmol) were added. The mixtures were stirred for 15 minutes and the solvent then removed with rotary evaporation followed by high vacuum. ^{31}P NMR: **11a**, δ 67.8, 66.5 (1:1); **11b**: δ 60.9, 57.3 (1:2).

Step 3. N-Phenylmaleimide (0.55 g, 3.2 mmol) and triethylamine (1 g, 10 mmol) were added to separate solutions of dibromides **11a** and **11b** in 6 mL of dry benzene. The reaction mixtures were stirred under nitrogen for several days at room temperature with monitoring by ^{31}P NMR spectroscopy to follow consumption of starting dibromide. The precipitated triethylamine hydrobromide was removed by filtration and washed with dry benzene. The solution filtrates were evaporated to dryness and used directly in the next step. ^{31}P NMR: **11a**, δ 79.2; **11b**, δ 80.8.

Step 4. To a solution of Diels-Alder adduct **12a** or **12b** in 10 mL of chloroform, 30 mL of a chloroform solution of m-chloroperbenzoic acid (Lancaster, 3.10 g, (50%), 9 mmol) was added dropwise, and each reaction mixture was stirred for 12 hours at room temperature. After confirming by ^{31}P NMR spectroscopy that consumption of the Diels-Alder adducts had occurred, solid KF (3 g, 52 mmol) was added for complexation of m-chlorobenzoic acid and unreacted m-CPBA. After 3 hours of stirring of the mixture, the solid was removed by filtration through Celite, and the filtrate was evaporated to dryness in vacuo to afford crude mixtures of isomers **1a-D** and **13a** (^{31}P NMR: δ 26.2 and 25.6, ratio 2:3) and **1b-D** and **13b** (^{31}P NMR: δ 25.6 and 24.5, ratio 5:2). Attempts were made to separate the isomers by column chromatography on Florisil (100–200 mesh) with elution by dichloromethane–hexane (4:1), dichloromethane and dichloromethane–methanol (19:1). However, the products remained as a mixture of isomers: **1a-D** (96 mg, 47% purity from ^{31}P NMR spectroscopy), **1b-D** (187 mg, 70% purity).

1a-D (96 mg) was mixed with 32 mg of **1a**, and recrystallization from chloroform–hexane solution gave **1a-D** with a lower content of deuterium. Yield 56 mg (0.16 mmol), mp 152–153°C. ^{31}P NMR: δ 25.6; ^{31}H NMR: δ 1.34 (3H, t), 1.93 (3H, d of d, J = 1.76 Hz, J = 5.8 Hz), 3.35–3.65 (~0.5H, m), 3.65–4.4 (2H, m), 5.17 (1H, d of d of d, J = 2.3 Hz, J = 4.0 Hz, J = 23.2 Hz), 6.10 (1H, m), 7.1–7.5 (5H, m). FABMS showed the product to contain 45.4% **D**.

The crude **1b-D** was recrystallized twice from ethyl acetate/ether to afford pure **1b-D**. Yield 33 mg, 0.09 mmol, mp 159–160°C. ^{31}P NMR: δ 24.3; ^{31}H NMR: δ 1.03 (3H, t), 1.85 (3H, d of d, J = 1.85 Hz, J = 4.7 Hz), 2.7–3.3 (2H, m), 5.15 (1H, d of d of d, J = 2.1 Hz, J = 3.8 Hz, J = 22.2 Hz), 6.14 (1H, d of t, J = 8.5 Hz), 7.0–7.5 (5H, m). FABMS showed the product to contain 91.8% **D**.

Adamantylamine Salt of Ethyl 1-Propyl Phosphate (**14**). A solution of O-ethyl N-adamantyl phosphoramidic acid (0.073 g, 0.28 mmol) in 5 mL of 1-propanol was kept in a closed ampule for 1 hour at 100°C. The solvent was stripped off; the residue was washed with ethyl ether and recrystallized from ethanol–ethyl acetate solution. Yield of **14** 0.063 g, (70%), mp 217.5–219°C. ^{31}P NMR: δ −0.56; ^{1}H NMR: δ 0.91 (3H, t); 1.23 (3H, t); 3.7–4.2 (4H, m); 7.4–9.4 (3H, OH, and NH). FABMS for [M^- − $AdNH_3$]: m/z = 167.05 (calcd. 167.09).

Measurements of Isotope Effects

Isotope effects were measured by the competitive method. Samples of 1,2-dichloroethane solutions of **1a** or **1b** (0.05 mol/L) and 1-propanol (0.25 mol/L) were sealed under argon in glass ampules (1 mL) and kept at 100°C. The reaction was quenched before completion at 0°C. Full conversion samples were processed to at least 10 half-lives.

For the hydrogen isotope effect measurements, N-phenyl-1,2-dihydrophthalimide **2** was isolated by column chromatography on silica gel (Merck) with

dichloromethane–hexane (2:1) as an eluent, followed by additional chromatography on a silica gel plate (Merck) with dichloromethane–ethyl acetate (10:1) solution (R_f = 0.5). Isopropyl alcohol was used for extraction from the silica gel.

In the case of oxygen isotope effect measurements, the solution containing at least 3 μM of ethyl 1-propyl phosphate was treated with 30 μM of 1-adamantamine, and the solution was left open until 1-adamantylamine salt **14** had precipitated quantitatively. The solution was stripped off, and the residual solid was washed with ether and dried.

Samples obtained in the foregoing ways were subjected to mass spectrometric analysis. The isotopic ratios were measured using a hybrid FAB—isotope ratio spectrometer MI 1201 E (PO Elektron, Ukraine). Samples of about 0.3 mg were dissolved in about 5 μL of 3-nitrobenzyl alcohol (for **2**) or thioglycerol (for **14**). From 1 to 2 μL of the solution was placed on the copper tip of the direct insertion probe.

The mean values of $[M^+ + 2]/[M^+ + 1]$ (for **2**-protonated positive ions) or $[M^- - AdNH_3 + 2]/[M^- - AdNH_3]$ (for **14** anions) isotopic ratios were obtained from up to 50 separate determinations, each being an average of 10 individual measurements with precision of ±0.15–0.25% for anions and ±0.25–0.4% for positive ions.

The kinetic isotope effects were calculated from the slope of linear dependence:

$$\ln(R_\infty - fR_p) = \ln R_\infty + (k_L/k_H)^{-1} \ln(1 - f) \quad (2)$$

where $y = \ln(R_\infty - fR_p)$ and $x = \ln(1 - f)$. R's are isotopic ratios of product (p) after fraction of reaction f and product after full conversion (∞).

Kinetic Measurements. Samples of solutions of **1a** or **1b** (0.05 M) and 1-propanol (0.25 M) in 1,2-dichloroethane were placed in NMR tubes with an external standard (Ph_3PO in DMSO-d_6) and kept in a thermostat at 100°C. At various time intervals, the tube was removed, cooled rapidly, and the ^{31}P NMR spectrum was recorded. The concentration of the remaining substrate was determined from the diminution of the ^{31}P NMR signal. The thermolysis of **1a** and **1b** was followed for more than two half-lives; the first-order constants of $(8.50 \pm 0.20) \cdot 10^{-5}$ s^{-1} and $(9.38 \pm 0.24) \cdot 10^{-5}$ s^{-1} were found, respectively.

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