(d, J = 10 Hz, H-5), 1.50, 1.39 (two *tert*-butyl groups), 1.24 (C-3 *tert*-butyl group), 0.97 (C-5 *tert*-butyl group); NMR (of **9b**) δ 7.36, 7.26 (aromatic H), 6.19 (d, J = 6.5 Hz, H-4), 3.59 (s, NCH_3), 3.32 (d, J = 6.5 Hz, H-5), 1.52, 1.39 (two *tert*-butyl groups), 1.25 (C-3 *tert*-butyl group), 1.17 (C-5 *tert*-butyl group).

Anal. Calcd for $C_{29}H_{43}NO_2$ (mol wt 437.67): C, 79.58; H, 9.90. Found C, 79.53; H, 9.93.

Base-Catalyzed Isomerization of 9 (10). Potassium *tert*-butoxide (60 mg) was added to a solution of **9** (219 mg, 0.5 mmol) in dimethyl sulfoxide (30 mL) and ethanol (3 mL) at 80 °C under nitrogen blanketing. The reaction mixture was kept at 80–85 °C under nitrogen for 80 min. Addition of water (15 mL) gave a colorless crystalline precipitate which was removed by filtration and recrystallized from aqueous ethanol: yield 180 mg (82%); mp 181–182 °C (lit.[2] mp 182–183 °C), no depression upon admixture of authentic[2] **10**.

Acid-Catalyzed Rearrangement of 6 in the Presence of Water (12). Trifluoroacetic acid (2 mL) was added to a solution of **6** (1.4 g, 3.2 mmol) in ethanol-free chloroform (5 mL) at room temperature. After 15 min, the green-fluorescent solution was diluted with a mixture of methanol (15 mL) and water (5 mL). After 45 min of stirring, the solution had turned colorless. Vacuum evaporation of solvents gave an oily residue which crystallized upon treatment with methanol. Recrystallization from aqueous methanol gave 1.1 g (73%) of colorless crystals: mp 195–196 °C; IR 3340 (s), 1680 cm^{-1} (s); UV (in ethanol) λ 218 nm ($10^{-3}\epsilon$ 29.5), 223 (29.0), 258 (16.6), 265 (sh, 13.0), 336 (5.1), 345 (sh, 4.7); NMR δ 7.65 (d, J = 2 Hz, 1 H), 7.55 (d, J = 2 Hz, 1 H), 5.96 (br m, NH), 2.81 (d, J = 4.5 Hz, NCH_3), 2.54 (t, J = 9.5 Hz, 1 H), 2.46 (d, J = 9.5 Hz, 1 H), 1.62 (d, J = 9.5 Hz, 1 H), 1.44 (s, 9 H), 1.33 (s, 9 H), 1.04 (s, 9 H), 0.86 (s, 9 H); ^{13}C NMR 199.7 (C=O), 173.6 ppm (NC=O).

Anal. Calcd for $C_{29}H_{45}NO_3$ (mol wt 455.68): C, 76.44; H, 9.95. Found: C, 76.28; H, 9.87.

Acknowledgment. We are gratefully indebted to Mr. Gunnar Svensson for technical assistance and to Mr. Reine Torberntsson and Mr. Kjell Andersson for their help with the NMR experiments.

Registry No. 2a, 60434-60-8; **2b**, 60434-61-9; **2c**, 60434-62-0; **3a**, 78591-95-4; **3b**, 78591-96-5; **3c**, 78591-97-6; **6**, 60434-70-0; **8**, 78624-41-6; **9**, 78591-98-7; **10**, 60434-67-5; **12**, 78591-99-8.

Lewis Acid Catalyzed Methanolysis of a Phosphate Triester

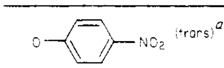
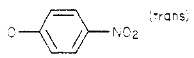
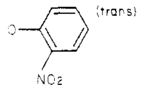
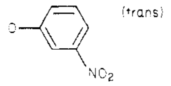
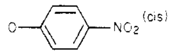
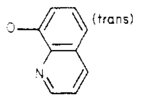
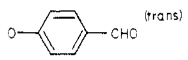
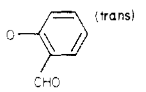
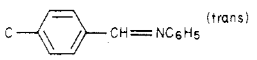
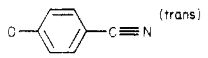
William S. Wadsworth, Jr.

Department of Chemistry, South Dakota State University, Brookings, South Dakota 57007

Received March 17, 1981

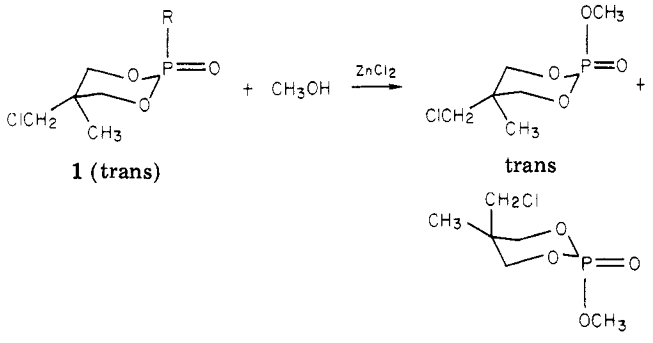
Trialkyl phosphates are both found in nature and used as commercial products. Because of their utility, it is of interest to determine those factors which influence their reactivity. In a recent publication,[1] we described the proton-catalyzed methanolysis of 2-substituted 5-(chloromethyl)-5-methyl-2-oxo-1,3,2-dioxaphosphorinan (1). We found that at low acid concentrations the configuration at phosphorus was retained while at elevated proton concentrations both retention and inversion occur, with inversion predominating. At low acid concentrations protonation takes place on phosphoryl oxygen, the most basic site. Displacement occurs via a pentavalent intermediate. At high concentrations additional protonation of the leaving group leads to both retention and inversion with

Table I. Methanolysis Catalyzed by Zinc Chloride

R	time for half-reaction, h[a,b]	% trans	% cis
	4[a]	40	60
	21[d]	45	55
	∞	NR[e] after 15 days	
		40	60
	insol in CH_3OH at room temp[c]	65	35
	>245 (42%)	100	0
	∞	NR	
	∞	NR	
	12	27	73
	3.6	46	54

[a] Solutions 0.1 M in ester and 0.1 M $ZnCl_2$. [b] Reactions run at room temperature. [c] Reactions run at reflux. [d] 0.05 M $ZnCl_2$. [e] NR, no reaction.

We are limited by the lack of solubility of most metal salts in methanol. Our work, therefore, was restricted to zinc chloride which in methanol is undoubtedly ionized and the cation solvated.[2] The system is relevant, for zinc ion is a common requirement for a number of enzymatic systems.[3]



1 (trans)

trans

cis

Methanolysis occurs readily in those cases where the leaving group is capable of complex formation with zinc ion (Table I). The product ratio, 60% inversion, is not unlike that found in proton catalysis at high acid concentrations. The ratio does not change appreciably at catalyst concentrations greater than 1 equiv but does tend to decrease at lower concentrations. A greater than equivalent amount of catalyst increases the initial rate of methanolysis only slightly. The reactions are not first

---

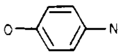
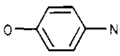
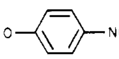
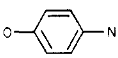
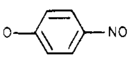
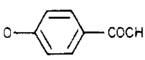
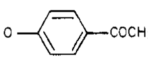
[1] Gehrke, S. H.; Wadsworth, W. S., Jr. *J. Org. Chem.* **1980**, *45*, 3921.

[2] Cotton, F. A., Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 599.

[3] Ochiai, Ei-Ichiro "Bioinorganic Chemistry"; Allyn and Bacon: Boston, MA, Chapter 13.

0022-3263/81/1946-4080$01.25/0

Table II. Effect of Cations on the Transesterification of Phosphate Triesters under Basic Conditions

R[b]	catalyst (1 equiv)	time for half-reaction, h	% inversion[a]	% retention[a]
	CH_3COONa[c]	97	0	100
	$Hg(C_2H_3O_2)_2$	190	27	73
	$Mg(C_2H_3O_2)_2\cdot4H_2O$	31	30	70
	$Zn(C_2H_3O_2)_2\cdot3H_2O$	7	58	42
	$Pb(C_2H_3O_2)_2\cdot3H_2O$	1.25	88	12
	$Mg(C_2H_3O_2)_2\cdot4H_2O$	38	48	52[d]
	$Pb(C_2H_3O_2)_2\cdot3H_2O$	3.4	87	13[d]

[a] Results to within ±2%. The percentages at 100% completion. [b] Solutions 0.1 M in ester. [c] Two equivalents used here. [d] Slight ring opening accompanied these reactions.

order in catalyst. Results suggest that 1 equiv of the divalent zinc ion is sufficient to complex with both the phosphoryl oxygen and the leaving group such that additional catalyst has little effect.

In those cases where the leaving group does not form a complex, room-temperature methanolysis either does not occur or occurs at a very low rate. Thus, the ester prepared from *p*-hydroxybenzaldehyde at room temperature does not react whereas after conversion to the imine it undergoes rapid methanolysis. The aldehyde does undergo methanolysis under reflux to give the typical ratio of isomers. The *p*-cyanophenyl ester is reactive, even more so than the *p*-nitro analogue. Results reflect the ability of solvated zinc ion to complex with trivalent nitrogen and to a lesser degree with carbonyl oxygen.[4] In contrast, the *p*-methoxyphenyl ester is recovered after 1 week at reflux. The methyl esters, the products of methanolysis, likewise are inert under all conditions. The fact that the *cis-p*-nitrophenyl ester gives methyl esters in a reciprocal ratio to the trans is, as in the case of proton catalysis, evidence that the ratios reflect kinetic control.

Unlike proton-catalyzed methanolysis, zinc chloride catalyzed methanolysis is not first order in ester. Rates decrease rapidly as the reaction proceeds. Methyl ester, the product, inhibits methanolysis by complexing more strongly than the reactant with zinc ion. Evidently, the strongest phosphoryl oxygen–zinc ion complexes are formed from those phosphates which do not have electron-withdrawing ligands. One equivalent of methyl ester added to zinc chloride solutions prior to addition of the *trans-p*-nitrophenyl ester inhibits methanolysis to the point where substitution is complete only after solutions have stood at room temperature for 3 months. In such a case, effective catalyst concentration is very low, and methanolysis proceeds only by retention. As with low proton concentrations, only the phosphoryl oxygen, the most basic site, must complex, leading exclusively to substitution via a pentavalent intermediate. The slow methanolysis, with retention, of the ester prepared from 8-hydroxyquinoline is indicative that in this case only complex formation through phosphoryl oxygen is effective. The *p*-methoxyphenyl ester, with its electron-donating substituent, added to methanol containing 1 equiv of zinc chloride prior to addition of the reactant completely inhibits methanolysis.

Methanolic solutions of the unreactive esters to which zinc chloride is added give, upon removal of solvent, amorphous products which defy crystallization. Lewis acids combine with phosphates in variable stoichiometric ratios.[5]

Due to their solubility in methanol, certain metal acetates were used to study the effect of metal ion catalysis under basic conditions (Table II). Base-catalyzed methanolysis in the absence of metal ions proceeds exclusively by retention.[6] Sodium ion does not alter the mechanism. The other ions listed have a dramatic effect, with lead ion being particularly effective in diverting the reaction pathway to inversion. It is reasonable to assume, as before, that the ions complex to varying degrees with the leaving group.[7] In this case relative rates are of little value, for metal acetates do not all ionize to the same extent in methanol.

In summary, it is apparent that the effectiveness of metal ions in promoting methanolysis is related to their ability to complex with potential leaving groups. In some cases phosphates can inhibit the reaction.

Experimental Section

^1H NMR spectra were recorded on a Perkin-Elmer R-12B spectrophotometer and chemical shifts measured relative to an internal tetramethylsilane standard with $CDCl_3$ as solvent. The ^1H NMR spectra of the methyl esters have been published.[8] Isomer ratios were obtained by integration of peaks due to 5-methyl hydrogens: cis methyl ester, 0.958 ppm; trans methyl ester 1.258 ppm.

Materials. The preparation and properties of the 2-substituted 5-(chloromethyl)-5-methyl-2-oxo-1,3,2-dioxaphosphorinans have been reported in a prior publication.[8] Methanol was distilled and the catalysts dried under vacuum before use.

Methanolysis of Phosphate Triesters. To 0.001 mol of ester was added 10 mL of a 0.1 M solution of catalyst dissolved in methanol. After being allowed to stand at room temperature, the solution was added to 50 mL of dilute HCl and the product

---

[4] Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; p 23.

[5] Apelblat, A.; Levin, R. *J. Inorg. Nucl. Chem.* **1979**, *41*, 115. Apelblat, A.; Levin, R. *J. Chem. Soc., Dalton Trans.* **1974**, 1476. Karayannis, N.; Mikulski, C.; Strocko, M.; Pytlewski, L.; Labes, M. *Inorg. Chim. Acta* **1974**, 91. Cobridge, D. E. C. "The Structural Chemistry of Phosphorus"; Elsevier: New York, 1974; p 221.

[6] To be submitted for publication.

[7] Previously, we showed that methanolysis of a 5-phenyl phosphorothioate can be diverted from the retention pathway to inversion by addition of Ag^+ or Hg^{2+} ions. Wadsworth, W. S., Jr.; Wilde, R. L. *J. Chem. Soc., Chem. Commun.* **1976**, 93.

[8] Wadsworth, W. S., Jr.; Larson, S.; Horton, H. L. *J. Org. Chem.* **1973**, *38*, 256. Bauman, M.; Wadsworth, W. S., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 6388.

extracted by means of two 25-mL portions of CH_2Cl_2. The combined extracts were washed with 0.1 M KOH and dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressure and the NMR of the residue taken without further purification.

This general procedure was used throughout and as determined from a controlled experiment had no effect on product ratios.

Isomer ratios and percent reactions were obtained by integrating peaks due to absorption by 5-methyl hydrogens. The hydrogens for each of the three components have different chemical shifts. Reactions were interrupted at different times and followed to at least 80% completion. From plots of several points, the times to reach 50% reaction were taken as $t_{1/2}$.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. *trans*-1 (R = *p*-$NO_2C_6H_4O$), 36912-38-6; *trans*-1 (R = *o*-$NO_2C_6H_4O$), 78609-79-7; *trans*-1 (R = *m*-$NO_2C_6H_4O$), 78609-80-0; *cis*-1 (R = *p*-$NO_2C_6H_4O$), 36912-37-5; *trans*-1 (R = 8-quinolinyloxy), 78609-81-1; *trans*-1 (R = *p*-$CHOC_6H_4O$), 78609-82-2; *trans*-1 (R = *o*-$CHOC_6H_4O$), 78609-83-3; *trans*-1 (R = *p*-$C_6H_5N=CHC_6H_4O$), 78609-84-4; *trans*-1 (R = *p*-CNC_6H_4O), 68666-60-4; $ZnCl_2$, 7646-85-7.

Kolbe Electrosynthesis of Alkanes with Multiple Quaternary Carbon Atoms

Norman Rabjohn* and G. W. Flasch, Jr.

Department of Chemistry, University of Missouri, Columbia, Missouri 65211

Received April 27, 1981

Quaternary carbons in alkanes have been shown to affect their physical properites, particularly melting point, viscosity, and density. Tetraalkylmethanes such as 13-decyl-13-heptyltritriacontane are liquids,[1] while the corresponding *n*-$C_{50}H_{102}$ melts at 92 °C.[2] Levina and coworkers have noted that highly branched alkanes of a C_9H_{20}–$C_{17}H_{36}$ structure with two or three quaternary carbon atoms, separated by a methylene group, generally have higher viscosities and densities and become vitrified at low temperatures, ca. −45 to −95 °C.[3]

In conjunction with another study, it appeared of interest to examine the properties of alkanes with two–four quaternary carbons, each substituted with two ethyl groups. The syntheses of 3,3,6,6-tetraethyloctane (**2**), 3,3,6,6,9,9-hexaethylundecane (**11**), and 3,3,6,6,9,9,12,12-octaethyltetradecane (**12**) were carried out as indicated in Scheme I. The Kolbe electrolyses were accomplished readily by means of a cell with a platinum gauze anode and a mercury cathode.[4] The electrolysis of 3,3-diethylpentanoic acid (**1**) afforded 81% of the normal Kolbe coupling product (**2**) plus a mixture of compounds of which **3**–**5** undoubtedly arose from carbonium ions formed by anodic oxidation of the free radicals which were intermediates of the electrolysis of the carboxylic acid.[4] They were separated by gas chromatography and their proposed identities are based on elemental and spectral analyses.

The formation of byproducts **3** and **4** may be ascribed to the oxidation of the 2,2-diethylbutyl radical to the corresponding carbonium ion which rearranged to the more stable tertiary 1,1-diethylbutylcarbonium ion. Coupling of the latter, or deprotonation, could have produced the compounds. Abstraction of a hydrogen atom on the 4-position of the 2,2-diethylbutanecarboxylate ion, followed by oxidation of the new radical to a carbonium ion and coupling of the ions, might have led to **5**. It is conceivable that the intermediate 2,2-diethylbutyl carboxylate radical coupled with the 2,2-diethylbutyl radical, and the resulting ester was transesterified with methanol to give **6**.[4a]

The crossed-coupling of **1** and **7**, which was prepared in situ by attack of methoxide ion on 3,3-diethyl-1,5-pentanedioic anhydride, gave four major products: **2**, **3**, **8**, and **9**, representing 77% of the reaction mixture. A number of non-Kolbe minor components were isolated and their identities are suggested from spectral data (see Experimental Section).

The ester **9** was saponified to the acid **10**, which was electrolyzed with **1**, and the desired hydrocarbons **11** and **12** as well as **2** resulted. No attempt was made to separate other components of the mixture.

The melting points of **2**, **11**, and **12** are 7–8, 39.5–41.5, and 77–79 °C, respectively, while the corresponding *n*-isomers melt at 18, 47.6, and 65.8 °C.[5] It is interesting that the C_{30} hydrocarbon (**12**) has a higher melting point than triacontane. 2,2,5,5,8,8,11,11-Octamethyldodecane has been reported to melt at 37–38 °C, while *n*-$C_{20}H_{42}$ has a melting point of 36.8 °C.[6] These four highly branched alkanes have the quaternary carbons separated by two methylenes, which apparently permit the substituent groups to pack readily into not severely hindered but compact arrangments. Molecular models seem to support this view.

Experimental Section

Materials. 3,3-Diethylpentanoic acid (**1**) was prepared by a previously described procedure.[7] The sodium salt of hydrogen methyl 3,3-diethyl-1,5-pentanedioate (**7**) was made in situ by causing sodium methoxide to react with 3,3-diethyl-1,5-pentanedioic acid anhydride which had been obtained by treating the corresponding diacid with acetic anhydride.[8] 3,3-Diethyl-1,5-pentanedioic acid was synthesized by the acid hydrolysis of 2,4-dicyano-3,3-diethylglutarimide;[9] the latter was prepared from ethyl 2-cyano-3-ethyl-2-pentenoate and cyanoacetamide by the method of McElvain and Clemens.[10]

Electrolysis of 1. In a 1-L resin pot, fitted with a mechanical stirrer, internal cooling coil, reflux condenser, stopcook, and a platinum gauze anode (6 × 7 cm), 2 cm from the mercury cathode, were placed 47.5 g (0.3 mol) of **1**, 65 mL (0.3 mol) of 25% sodium methoxide in methanol, and 300 mL of anhydrous methanol. A direct current of 120 V and 13.7 amp was applied until the voltage and amperage reached a steady state and the evolution of gas had ceased. The reaction was stopped after 90 min by draining the mercury cathode while the potential was still applied. The methanol was removed by distillation, and the residue was dissolved in Et_2O, washed with 10% NaOH, and dried (Na_2SO_4). After removal of the Et_2O, the residue was distilled through a spinning band column to give three fractions: bp −50 °C (4.4 mm), 6.7 g; −114 °C (4 mm), 13.3 g; 114 °C (1.4 mm), 13.5 g; and residue, 2.1 g. The components of the fractions were isolated by prepa-

---

[1] Rabjohn, N.; Phillips, L. V.; DeFeo, R. J. *J. Org. Chem.* **1959**, *24*, 1964.

[2] Carothers, W. H.; Hill, J. W.; Kirby, J. E.; Jacobson, R. A. *J. Am. Chem. Soc.* **1930**, *52*, 5279.

[3] Levina, R. Y.; Daukshas, V. K. *Vestn. Mosk. Univ., Ser. Mat., Mekh., Astron., Fiz. Khim.* **1959**, *14*, 221 (*Chem. Abstr.* **1960**, *54*, 19455c).

[4] For leading references, see Baizer, M. M., Ed. "Organic Electrochemistry"; Marcel Dekker: New York, 1973; Chapter 13. Acknowledgment is made to a reviewer for this suggestion.

[5] Rappoport, Z., Ed. "Handbook of Tables for Organic Compound Identification", 3rd ed.; Chemical Rubber Co. Press: Cleveland, OH, 1967; p 8.

[6] Zakharova, A. I.; Il'ina, G. D.; Murashov, G. M. *Zh. Obshch. Khim.* **1955**, *25*, 1968 (*Chem. Abstr.* **1956**, *50*, 8439c).

[7] Rabjohn, N.; Phillips, L. V.; Stapp, P. R. *J. Chem. Eng. Data* **1962**, *7*, 543.

[8] Vogel, A. I. *J. Chem. Soc.* **1934**, 1758.

[9] Birch, S. F.; Kon, G. A. R. *J. Chem. Soc.* **1923**, *123*, 2440. Farmer, H. H.; Rabjohn, N. "Organic Syntheses", Collect. Vol. 4, Wiley: New York, 1963; p 441.

[10] McElvain, S. M.; Clemens, D. H. "Organic Syntheses", Collect. Vol. 4; Wiley: New York, 1963; p 662.

0022-3263/81/1946-4082$01.25/0