Table II. Vicinal Cyanohydrins Obtained by Ring Fragmentation.

^{a} Employing an excess of 2% Na–Hg in wet THF at 20 °C. Yields refer to isolated products. ^{b} We thank Miss C. L. Gualtieri for preparing a standard sample of this compound.

Table III. Nucleophilic Substitution Products

substrate	nucleophile	product **18**	yield, %
6	LiOMe^a	n = 3, Nu = OMe	82
6	KCN^b	n = 3, Nu = CN	87
7	NaBH$_4$^{c}	n = 4, Nu = H	51
7	LiOMe^a	n = 4, Nu = OMe^d	88

^{a} Refluxing MeOH, 1 h. ^{b} Me$_2$SO, 40 °C, 48 h. ^{c} i-PrOH, 80 min. ^{d} We thank Mr. S. A. Hardinger for carrying out a preliminary investigation.

oxime **2** (1.34 g, 5.06 mmol), CH$_2$Cl$_2$ (8.0 mL), and cyclohexene (8.1 g, 99 mmol) was added dropwise over 3 h to a mixture of 1.0 M aqueous sodium carbonate (8.0 mL) and cyclohexene (8.1 g, 99 mmol). The crude product was chromatographed (silica gel, CH$_2$Cl$_2$ elution) to give dibenzenesulfonylfurazan oxide (99 mg, 11% yield) followed by pure cycloadduct **7** (1.02 g, 76% yield). A vigorously stirred THF (17 mL) solution of the cycloadduct (0.59 g, 2.23 mmol) was treated with water (0.52 mL) and 2% Na–Hg (7.37 g, 6.4 mg-atoms of Na). After 1 h, additional water (0.26 mL) and 2% Na–Hg (3.71 g) were added. Kugelrohr distillation of the crude product afforded 0.24 g (86% yield) of pure vicinal cyanohydrin **15**:[13] bp 130–40 °C at 0.1 Torr; mp 32.5–34 °C; IR (melt) 2.75–3.15 (br, OH), 4.46 μ (C≡N); NMR (CDCl$_3$) δ 3.75 (m, 1 H, CHOH), 3.03 (m, 1H, CHCN), 2.6 (s, 1 H, D$_2$O exchanges, OH), 1.3–2.2 (m, 8 H).

The carbon–nitrogen double bond of isoxazolines undergoes nucleophilic attack resulting in substitution if a suitable leaving group is attached at carbon.[14] Consequently, the reaction of cycloadducts **6** and **7** with various nucleophiles was examined in the hope that substitution would occur. Treatment with lithium methoxide, sodium cyanide, and sodium borohydride leads readily to the corresponding substitution products (Table III). These reactions, in conjunction with the cycloaddition process, constitute an alternative to direct reaction of the alkene with fulminic acid,[2b] cyanogen *N*-oxide,[15] or the as yet unknown methoxynitrile oxide. Consequently, benzenesulfonylnitrile oxide is a useful synthetic equivalent to other members of the class. This matter, as well as the broad application of benzenesulfonylnitrile oxide to synthetic problems, is under further investigation.

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(6) The procedure was as follows. A solution of Br$_2$ (4.03 g, 25.2 mmol) in CH$_2$Cl$_2$ (100 mL) was added dropwise over 30 min to a cold (0–5 °C) mixture of α-nitro sulfone **3** (5.04 g, 25.1 mmol), NaOAc (8.43 g), and CH$_2$Cl$_2$ (100 mL). The resulting crude product was a 7:86:7 mixture of non-, mono-, and dibrominated α-nitro sulfone. Without purification this was dissolved in ether (anhydrous, 40 mL) and the solution cooled (−10 °C). Treatment with five 10-mL portions of 0.55 M ethereal CH$_2$N$_2$ over 15 min effected complete conversion to the nitronic ester (TLC). The resulting solution was *partially* stripped under reduced pressure (*Caution:* complete stripping may lead to vigorous decomposition) and the solvent replaced by CH$_2$Cl$_2$ (100 mL). Refluxing for 15 min resulted in complete destruction of the nitronic ester. The oily crude product crystallized (with difficulty) from a concentrated CH$_2$Cl$_2$–hexanes solution. Recrystallization gave 2.03 g (31% yield) of crystalline **2**: mp 101–102 °C; IR (KBr) 2.85–3.2 (br, OH), 6.21 and 6.32 (C=N and C=C), 7.24, 7.51, and 8.64 μ (sulfone).
(7) Triethylamine can be used instead but only with the more reactive alkenes.
(8) Tetramethylethylene does not react with typical nitrile oxides. It can react in low yield with mesitonitrile oxide (which dimerizes with extreme difficulty owing to the large size of the aryl substituent), but this is an isolated instance: Ch. Grundmann, H.-D. Frommeld, K. Flory, and S. K. Datta, *J. Org. Chem.*, **33**, 1464 (1968).
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(13) The trans isomer of **15**, prepared by treating cyclohexene oxide with KCN, is clearly a different compound: mp 46–47 °C (lit.^{4a} mp 46–47 °C); IR (melt) 2.75–3.15 (br, OH), 4.46 μ (CN); NMR (CDCl$_3$) δ 3.6 (M, 1 H, CHOH), 3.18 (s, 1 H, D$_2$O exchanges, OH), 1.2–2.5 (m, 9 H, CHCN and other ring H).
(14) P. A. Wade, *J. Org. Chem.*, **43**, 2020 (1978). (b) See also R. Bonnett, "The Chemistry of the Carbon–Nitrogen Double Bond", S. Patai, Ed., Interscience, New York, 1970, p 597.
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Reactions of Zirconium Atoms with Alkanes: Oxidative Additions to Carbon–Hydrogen and Carbon–Carbon Bonds

Sir:

The activation of saturated hydrocarbons by molecular species has been one of the important goals of organometallic chemistry in recent years. We report here the oxidative addi-

Table I. Products of Zirconium–Isobutane Reaction

product	rel yield/ mmol of Zr	product	rel yield/ mmol of Zr
	Warmup		
H_2	0.480	CH_4	0.005
	Hydrolysis with H_2O		
H_2	1.500	C_3H_8	0.038
CH_4	0.121	i-C_4H_8	0.144
C_2H_6	0.043	i-C_4H_{10}	0.190
C_3H_6	0.005	$Zr(OH)_4$	1.000

Table II. Products of Zirconium–Neopentane Reaction

product	rel yield/ mmol of Zr	product	rel yield/ mmol of Zr
	Warmup		
H_2	0.240	CH_4	0.012
	Hydrolysis with H_2O		
H_2	0.820	i-C_4H_8	0.014
CH_4	0.094	i-C_4H_{10}	0.045
C_2H_6	0.009	C_5H_{12}	0.250
C_3H_6	0.001	$Zr(OH)_4$	1.000
C_3H_8	0.010		

Table III. Results of Transition Metal Survey with Isobutane

metal	yield[a]	metal	yield[a]
zirconium	54.7	nickel	0.3
vanadium	0.9	cobalt	0.1
titanium	10.0	copper	0
chromium[b]	0.3	molybdenum	0.2
manganese	0.2	tungsten	2.7
iron	0.3		

[a] Millimoles of hydrocarbons/millimoles of metal deposited × 100 disregarding all hydrogen formed during hyrolysis. [b] Evidence of carbide formation not reflected in hydrocarbon yields.

Scheme I

$$Zr + \text{neopentane} \longrightarrow HZrCH_2C(CH_3)_3 \quad \mathbf{1}$$

$$\longrightarrow H_3CZrC(CH_3)_3 \quad \mathbf{2}$$

$$H_3CZrC(CH_3)_3 \longrightarrow H_3CZr\overset{CH_2}{\underset{H}{\diagup\diagdown}}C(CH_3)_2 \quad \mathbf{3}$$

tion of zirconium atoms to carbon–hydrogens and carbon–carbon bonds of alkanes at cryogenic temperatures, a behavior which is unique among the metal atoms studied up to this time.

We have vaporized zirconium metal from a tungsten wire[1] at ~2500 K and cocondensed the metal atoms with vapors of research grade isobutane and neopentane at 77 K to form a 100:1 alkane to metal matrix. The codeposition is carried out in a large, thin-walled, reactor vessel, described elsewhere[2] at a pressure of <4 × 10⁻⁶ Torr to preclude the possibility of gas-phase collision and substrate pyrolysis. Light brown matrices result which turn black shortly before the hydrocarbon matrix melts. Excess hydrocarbon is removed with continuous pumping as the matrix warms, with simultaneous collection of noncondensibles; slow evolution of further small amounts of hydrogen and methane continues for ~1 h after the black matrices reach room temperature, and then ceases. The analyses of these noncondensibles is given in Tables I and II; it is mainly hydrogen. The recovered isobutane or neopentane contains only impurities which were present in the starting materials.

The black solid is insoluble in hydrocarbon solvents and does not liberate hydrocarbons when exposed to hydrogen; however, the dry solid is rapidly hydrolyzed by water or alcohol to yield hydrogen, the original hydrocarbon, smaller amounts of lower molecular weight hydrocarbons, and zirconium(IV) hydroxide or alkoxide. Tables I and II list the relative yields of both hydrogen and hydrocarbon per millimole of zirconium deposited in the reaction zone.

The variety and distribution of hydrocarbons produced on hydrolysis suggests that two competing reactions occur in the initial formation of the organozirconium species (Scheme I). In the case of neopentane, zirconium atoms can oxidatively add across a carbon–hydrogen bond to yield **1** or alternately across a carbon–carbon bond to produce **2**.

Since **1** has no β hydrogens, it should survive intact on warming to room temperature. **2** however has nine β hydrogens and can undergo additional reaction with the coordinatively unsaturated zirconium to form **3**.

To test this hypothesis, a series of experiments were undertaken in which the zirconium–neopentane solid was vacuum dried of all excess substrate and then hydrolyzed with 99.8% D_2O. The hydrolysis products were separated by gas chromatography and analyzed by mass spectrometry; 80% of the

hydrogen evolved on hydrolysis was HD, the remainder D_2 giving strong support for the presence of a zirconium hydride species. The C_2, C_3, and C_4 hydrocarbon species were highly deuterated. The neopentane on the other hand was exclusively monodeuterated. The lack of a polydeuterated neopentane and the presence of hydrogen and olefin products in the same reaction mixture argues against the possibility of an active metal surface catalyzing a protium–deuterium exchange between the D_2O and the hydrocarbon products.

If the hydrogen and methane evolved during warmup are each the result of the loss of two groups, and the hydrolysis products one group, the number of fragments accounted for are 3.5 and 3.0 per zirconium, for isobutane and neopentane, respectively. These numbers approach the value of 4.0 which might be expected for a 4b metal atom. This suggestion is supported by the formation of polydeuterated fragmention products and olefin on hydrolysis with D_2O.

In light of the work done by Ozin[3] in which vanadium atoms in isobutane were observed to diffuse to form divanadium at 57 K, it is highly unlikely that zirconium could survive as an isolated atomic species at temperatures above 77 K. Therefore the possibility of the zirconium alkane reaction occurring during matrix warmup is remote. What is more likely is that the zirconium atoms react immediately upon impact with the rapidly condensing alkane surface to form **1** and **2**. These species, because of their size, could not diffuse rapidly at 77 K and should survive up to the melting point of the alkane where the organozirconium species could agglomerate into an extended three-dimensional structure. This would account for the transformation of the initially formed brown matrix to a black substance which is stable at room temperature.

We have conducted a survey of a variety of transition metals in isobutane using the same experimental procedures. Table III lists the results, comparing the total hydrocarbon yield vs. total metal deposited in the reaction zone. Of these elements, zirconium is unique. Only titanium exhibits any substantial reactivity with isobutane under these conditions.[4]

We are currently extending this work to include other hydrocarbon substrates and other group 4b metals.

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References and Notes

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Pentacoordinate Intermediates in Displacement at Sterically Hindered Phosphorus. A Correction

Sir:

A central problem in the fundamental understanding of reactions at phosphorus is the question of whether pentacoordinate intermediates exist along the reaction pathway. As part of a series of investigations on displacement at phosphorus,[1] we have utilized phosphinates as substrates in order to have a single functional group (eq 1). A preference for asso-

$$R-\overset{\overset{O}{\|}}{\underset{\underset{R}{|}}{P}}-X \ + \ HY \ \longrightarrow \ R-\overset{\overset{O}{\|}}{\underset{\underset{R}{|}}{P}}-Y \ + \ HX \qquad (1)$$

$$\underset{1}{} \qquad\qquad\qquad \underset{2}{}$$
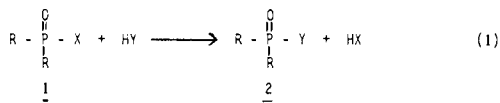
ciative pathways in displacement at phosphorus was clearly demonstrated by studies of the rate of solvolysis of phosphinyl chlorides, $R_2P(O)Cl$, and the behavior of phosphinic acids, R_2PO_2H, in strong acid.[2,3] Since there are a large number of stable pentacoordinate phosphorus compounds, it seems reasonable that the lowest energy associative pathway for displacement at phosphorus will involve an addition–elimination mechanism through a pentacoordinate intermediate. With cyclic phosphates, rate phenomena indicate that conformationally mobile pentacoordinate species are intermediates in displacement reactions,[4] and a large number of cyclic, pentacoordinate adducts have been isolated and investigated,[5] but, with acyclic phosphorus substrates, it has been difficult to gain clear evidence for pentacoordinate intermediates.

Some time ago, we called attention to an induction period in the rate of alkaline hydrolysis (at 75 °C in 60:40 dimethoxyethane–water) of methyl diisopropylphosphinate (**1a**, R = $CH(CH_3)_2$, X = OCH_3), and we suggested that this might be explained by slow development of a steady-state concentration of a pentacoordinate intermediate with this sterically hindered ester.[1,6] However, when we tried to fit the experimental observations by numerical integration and analogue computation[7] to the expected kinetic scheme, **1** + HO^- $\rightleftharpoons$ **1** $\rightarrow$ products, we could not find an adequate fit. This led us to additional experiments which we now report.
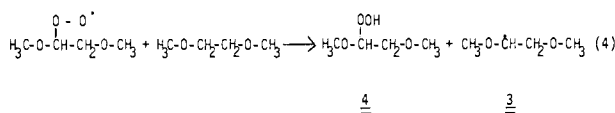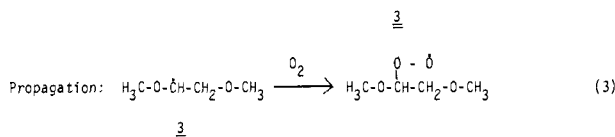
NMR spectroscopic observation of **1a** and the reaction products was utilized because of the highly diagnostic features: **1a** has an OCH_3 doublet and a CCH_3 octet (nonequivalent CH_3's and PCCH and HCCH couplings). At 75 °C in alkaline 60:40 dimethoxyethane-d_{10}:D_2O (or in basic D_2O) over periods during which HO^- had been consumed in the earlier reported experiments,[1,6] little decrease in the OCH_3 doublet was observed. At 100 °C in alkaline D_2O, the OCH_3 doublet

did disappear and the CCH_3 octet became a quartet consistent with hydrolysis giving $R_2PO_2^-$.[8] These results demonstrated that the consumption of HO^- observed earlier at 75 °C in dimethoxyethane–water must be due to some other reaction than hydrolysis of the phosphinate ester.
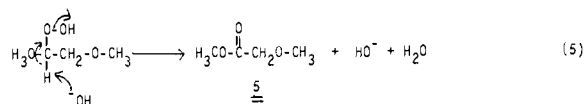
When the same reaction in dimethoxyethane–water was followed titrimetrically at 75 °C, but with ratios of ester:base being 1:2 and 1:4, both experiments gave induction periods though of varying duration. There was an exponential increase in the rate of consumption of base toward the end of the reaction and more than 1 equiv of HO^- was consumed; this observation is consistent with oxidation of the solvent by a free-radical, chain process. This hypothesis was supported by the fact that, when the reactions were done under a nitrogen atmosphere, there was no consumption of base. Furthermore, the reaction mixtures containing dimethoxyethane gave positive tests for the presence of peroxides using catechol. In contrast to the induction periods observed in dimethoxyethane–water, in water the reaction of methyl diisopropylphosphinate (**1a**) with base at 100.1 and 120.1 °C followed clean second-order kinetics with no induction period. The reaction was followed titrimetrically and NMR was used to identify the reaction as hydrolysis. The rate constants were 2.8×10^{-4} M^{-1} s^{-1} and 5.3×10^{-5} M^{-1} s^{-1} at 120.1 and 100.1 °C, respectively. The corresponding activation parameters are $\Delta H^{\ddagger} = 23.6$ kcal/mol, $\Delta G^{\ddagger} = 29.3$ kcal/mol, and $\Delta S^{\ddagger} = -15$ eu.

Because the reactions in dimethoxyethane–water were carried out in volumetric flasks which were opened to remove aliquots, the solution was exposed to oxygen leading to the formation of peroxides and consequent autoxidation[9,10] of dimethoxyethane.

A reasonable explanation involves a chain mechanism for oxidation (eq 2-4) in which the observed initiation period in-

Initiation: $R\cdot + H_3C-O-CH_2-CH_2-O-CH_3 \longrightarrow H_3CO-\overset{\cdot}{C}H-CH_2-O-CH_3 + RH$ (2)
$$\underset{3}{}$$

Propagation: $H_3C-O-\overset{\cdot}{C}H-CH_2-O-CH_3 \overset{O_2}{\longrightarrow} H_3C-O-\overset{\overset{O-\dot{O}}{|}}{C}H-CH_2-O-CH_3$ (3)
$$\underset{3}{}$$

$H_3C-O-\overset{\overset{O-O\cdot}{|}}{C}H-CH_2-O-CH_3 + H_3C-O-CH_2-CH_2-O-CH_3 \longrightarrow H_3CO-\overset{\overset{OOH}{|}}{C}H-CH_2-O-CH_3 + CH_3-O-\overset{\cdot}{C}H-CH_2-O-CH_3$ (4)
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \underset{4}{} \qquad\qquad\qquad \underset{3}{}$$

volves the generation of the radical **3** which is stabilized by both α- and β-oxy substituents.[9] The product hydroperoxide **4** would be expected to be reactive with base,[10,11] resulting in formation of the ester **5** (eq 5) which would consume base through hydrolysis.

$$H_3C\overset{\overset{O\overset{\frown}{O}H}{|}}{\underset{\underset{H}{|}}{C}}-CH_2-O-CH_3 \longrightarrow H_3CO-\overset{\overset{O}{\|}}{C}-CH_2O-CH_3 + HO^- + H_2O \qquad (5)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \underset{5}{}$$

Therefore, our previously reported observations are, regrettably, in error; the alkaline hydrolysis of **1a** in H_2O shows no induction period and no kinetic evidence for a pentacoordinate intermediate. The apparent induction period in hydroxide consumption appears to be due to oxidation of the solvent, dimethoxyethane.

References and Notes

(1) See R. D. Cook, C. E. Diebert, W. Schwarz, P. C. Turley, and P. Haake, *J. Am. Chem. Soc.*, **95**, 8088 (1973).