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Hydrogenation of 4-Substituted Biphenyls

Masahiro Minabe,* Kousuke Watanabe, Yooichi Ayabe, Masaaki Yoshida, and Takashi Toda

Department of Industrial Chemistry, Faculty of Engineering, Utsunomiya University, Ishiicho, Utsunomiya 321, Japan

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Hydrogenations of 4-hydroxy- (**1a**), 4-methoxy-, and 4-methylbiphenyls were carried out in the presence of Raney nickel (R–Ni), palladium-on-carbon (Pd–C), or platinum as catalysts under relatively mild conditions. The reaction rates depend primarily on the catalysts and less on the substrates. Hydrogenation with Pd–C or Pt took place predominantly in the phenyl ring, independent of the substituent. On the other hand, hydrogenation with R–Ni caused reduction mainly in the substituted aromatic ring. Hydrogenation of the phenol, **1a**, using R–Ni afforded predominantly *trans*-4-phenylcyclohexanol in preference to the cis isomer, differing from the other reactions examined.

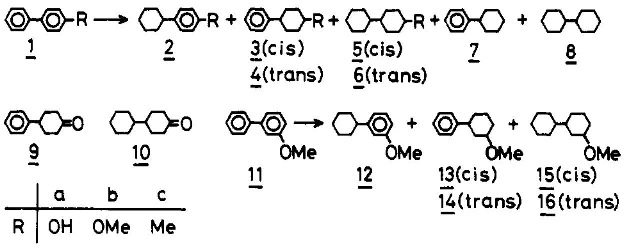
Partially hydrogenated aromatic hydrocarbons are of interest as synthetic intermediates,[1] as hydrogen-donor solvents in coal liquefaction,[2] and because of their potentially carcinogenic properties.[3] Catalytic hydrogenation of aromatic hydrocarbons has been investigated extensively from both stereochemical and mechanistic viewpoints.[1,4]

During the course of the studies on the hydrogenations of pyrene[5] and 4*H*-cyclopenta[*def*]phenanthrene,[6] we have recognized the necessity for establishment of the hydrogenation behavior of substituted biphenyls as a fundamental problem of polycyclic aromatic hydrocarbon chemistry. In this paper, we deal with the hydrogenations of phenol **1a**,[7] ether **1b**,[8] and hydrocarbon **1c**[9] (Scheme I).

Hydrogenation of **1a** has been carried out by using Raney nickel (R–Ni),[7,10–12] copper chromite,[7] palladium-on-carbon (Pd–C),[13] or platinum-on-carbon[13] as catalysts to give phenol **2a**,[7] *cis* **3a**[11] and trans alcohol **4a**,[11] *cis* **5a**[11] and trans alcohol **6a**,[11] and hydrogenolysis products **7** and **8**. Reduction of **1b** has been scarcely investigated except for hydrogenation[7] using R–Ni and the Birch method.[14] Catalytic reduction of **1c** has not been previously reported.

Prior investigations considered only the functions of catalyst, temperature, and pressure. However, it is conceivable, and even likely, that these reactions might change over the course of time. One of interest is the cis/trans ratio of the products: only trans isomers **4a** and **6a** have been isolated by the hydrogenation of **1a** with R–Ni.[7,10,11] A second point of interest is which of the two rings is first hydrogenated. The catalytic reduction of alkyl-substituted benzenes is generally slower than that of parent benzene due to steric hindrance (catalytic hindrance).[15,16] On the other hand, heteroatom-bearing biphenyls such as **1a** or **1b** are adsorbed at the heteroatoms by the "anchor effect", which might be expected to favor preferential initial hydrogenation in the *p*-phenylene ring moiety.[11,16]

Scheme I



This paper deals with hydrogenations of **1a**, **1b**, and **1c** with respect to the product distribution as a function of reaction time under relatively mild conditions, at 50 °C under hydrogen pressure of 5 kg cm^{-2} (1 kg cm^{-2} = 98066.5 Pa). The reaction of ketone **9** was determined to give primarily either ketone **10** or alcohols **3a** and **4a**.[10,17] Catalytic reduction of ether **11**[18] was also carried out in order to clarify the substituent effect.[7] This paper sheds light on the reaction pathway and reveals the reaction conditions necessary to obtain specific hydrogenated biphenyls.

Results and Discussion

Hydrogenation of **1a** in the presence of R–Ni (W-7) was carried out in ethanol to afford **2a**, **3a**, **4a**, **5a**, and **6a**. Graph 1 (Figure 1) shows the relation of the ratio of each product vs. reaction time. The product distribution was not changed significantly either by the amount of the catalyst (0.5–2.0 g depending on alloy) or by the preparative method of catalyst (W-7 and W-4). Change of solvent from ethanol to cyclohexane slowed the reaction rate but did not alter the product distribution.

Hydrogenation of **1a** in the presence of Pt in ethyl acetate was determined to give **2a**, **3a**, **4a**, **5a**, **6a**, **7**, **8**, **9**, **10**, and a trace amount of biphenyl as shown in graph 3 (Figure 1). When the reaction was carried out in some media, the trends were similar to those in ethyl acetate, except that the reaction was slower, in the order AcOH, EtOAc, EtOH, EtOH–NEt_3, cyclohexane.

Hydrogenations of **1b** with R–Ni in ethanol, with Pd–C in ethyl acetate, and with Pt in ethyl acetate were carried out to afford **2b**, **3b**, **4b**, **5b**, **6b**, **7**, and **8** as shown in graphs 4–6 (Figure 1), respectively. Hydrocarbon **1c** was hydro-

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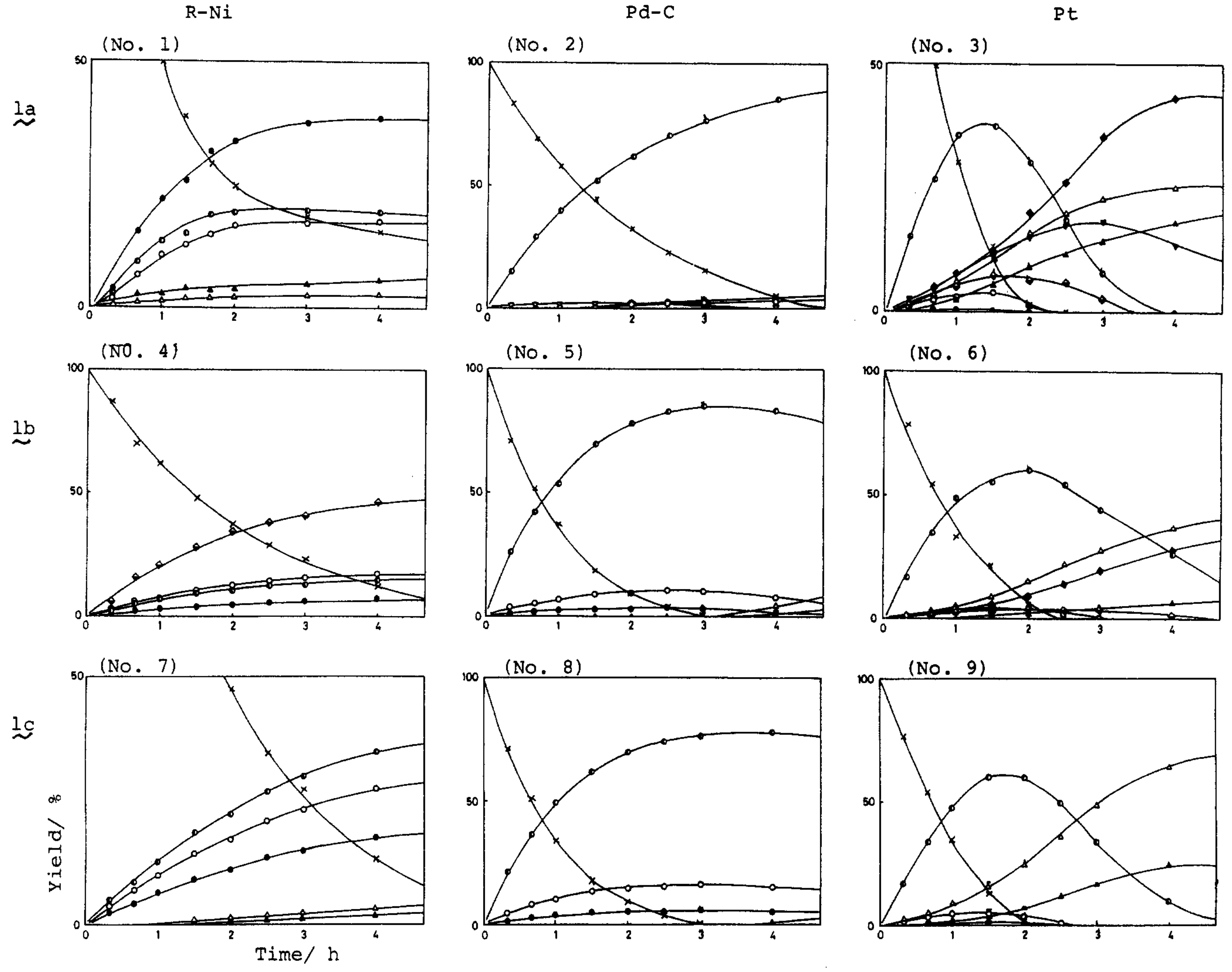

Figure 1. Time–course patterns on hydrogenation of **1a**, **1b**, and **1c**: (×) **1**; (◐) **2**; (○) **3**; (●) **4**; (△) **5**; (▲) **6**; (◈) **7**; (◆) **8**; (▽) **9**; (▼) **10**.

Table I. Rate Constant and Relative Selectivity on the Hydrogenation of 1, 9, and 11 at Initial Stage

reactant	cat.	solv	rate constant,[a] mol s^{-1} g-cat.$^{-1}$	relative selectivity, mol %								
				2	3	4	5	6	7	8	9	10
1a	R–Ni	EtOH	1.9×10^{-7}	27	22	41	4	6				
1b[b,c]	R–Ni	EtOH	4.8×10^{-8}	28	34	11	<1	<1	25			
1c	R–Ni	EtOH	3.1×10^{-8}	41	36	23	<1	<1				
9	R–Ni	EtOH	4.2×10^{-7}		47	50						3
11	R–Ni	EtOH	6.2×10^{-8}	17 (**12**)	49 (**13**)	13 (**14**)	2 (**15**)		19			
1a	Pd–C	EtOAc	8.5×10^{-8}	89	2	2	<1	<1			3	<1
1b[c]	Pd–C	EtOAc	1.1×10^{-7}	87	10	3	<1	<1	<1	<1		
1c	Pd–C	EtOAc	7.5×10^{-8}	76	17	7	<1	<1				
9	Pd–C	EtOAc	8.8×10^{-8}		5	82		2				11
11[d]	Pd–C	EtOAc	2.2×10^{-7}	21 (**12**)	48 (**13**)	23 (**14**)			1			
1a[e]	Pt	EtOAc	1.4×10^{-5}	58	6	2	6	2	6	8	3	8
1b	Pt	EtOAc	1.4×10^{-5}	79	5	1	7	1	3	5		
1c	Pt	EtOAc	1.5×10^{-5}	77	10	2	9	2				
9	Pt	EtOAc	7.9×10^{-6}		3	4	1	2	2			88
11	Pt	EtOAc	1.4×10^{-6}	77 (**12**)	4 (**13**)	2 (**14**)	5 (**15**)	2 (**16**)	4	6		

[a] Each weight of R–Ni, Pd–C, or Pt as catalyst is based on nickel–aluminum alloy (50%), Pd–C (5%) itself, or platinum oxide, respectively. [b] In addition, 2% biphenyl was confirmed. [c] Trace amounts of **5a** and **6a** were observed. [d] A small amount of 3-phenylcyclohexanone was detected. [e] Also, biphenyl (1%) was estimated.

genated under similar conditions by using R–Ni (graph 7, Figure 1), Pd–C (graph 8), or Pt (graph 9) to yield **2c**, **3c**, **4c**, **5c**, and **6c**.

The rate constant of the conversion of each substrate was roughly estimated from the time–course relation in Figure 1 on the basis of the assumption[15] that the reaction followed zero-order kinetics in substrate in its first stage. The relative selectivity of each product at the initial step was determined by the known procedure[19,20] as shown in Table I.

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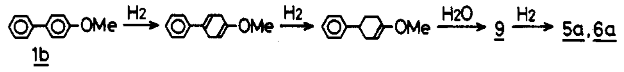
Scheme II



The rate of hydrogenation seems to be affected by the character of the catalyst more than by the substituent. For example, the reaction rate of **11** is faster than that of **1b** in the presence of R–Ni or Pd–C, but that of **11** in the presence of Pt diminishes to $^1/_{10}$ that of **1b**. The distribution on the reaction of **11** with R–Ni or Pt shows a trend similar to that of **1b**. The effect of the position of the substituent is only observed in the reaction with Pd–C; the distribution of electronic charge in the substrates may affect the hydrogenation using Pd–C.

The hydrogenation of monosubstituted benzenes such as **3** or **4** is generally more facile than that of 1,4-disubstituted benzenes **2**.[15] Therefore, it is reasonable to assume at the initial stage that most of the secondary products, **5–8**, and ketones **9** and **10** are formed from **3** and **4**, but not from **2**. The relative selectivity of **2** (Table I) shows the ratio of hydrogenation to the monosubstituted benzenes. The overall trends in the presence of Pd–C or Pt are that the hydrogenation occurs mainly at the phenyl moiety of the substituted biphenyls due to the difference of magnitude of catalytic hindrance between phenyl and *p*-phenylene groups.

On the other hand, hydrogenation using R–Ni occurs mainly at the *p*-phenylene moiety of the molecule.[10,11] The anchor effect affects only a narrow range in the case of R–Ni as catalyst; relatively low yields of **2a** and **2b** (27–28%), compared with that of **2c** (41%), are possibly because of the anchor effect. The hydrogenations using Pd–C seem not to be in agreement with regard to the catalytic hindrance and the anchor effect, and similar disagreement has been found in the reaction of 2-substituted naphthalenes.[20]

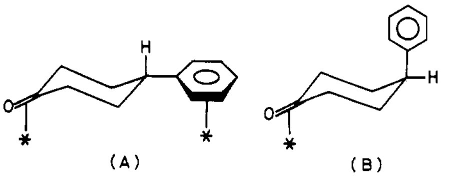
Hydrogenolysis was observed in the reactions of alcohol and ethers. The fission of ether takes place mainly to give hydrocarbons and methanol.[13] The alcohols **5a** and **6a** in the reaction products of **1b** are postulated[20] to form via enol ether intermediates to give **9** and/or **10**, followed by successive hydrogenation as shown in Scheme II.

The cis/trans ratio of isomers, that is **3**:**4** and **5**:**6**, changes slightly with the reaction time, possibly because of the successive hydrogenation and hydrogenolysis of each product. The overall trends show cis isomers forming more than trans on the hydrogenations, except for **1a** with R–Ni and for the hydrogenations of **9**. This is in accord with expectation for cis addition by kinetic control under mild conditions.[21,22] Ethers **13** and **15** may be more stable thermodynamically than **14** and **16**, respectively,[22] which could additionally assist the formation of cis isomers.

The formation of trans isomers is attributed to isomerization during the hydrogenation.[21,23] In the case of reactions of **1a**, presumably part of the trans isomers may be formed through the possible intermediate **9** (Scheme II) (cf. ref 22).

The pattern of catalytic reduction of **9** differs significantly according to the catalyst used. The phenyl group is easily hydrogenated in the presence of Pt.[17] On the other hand, the carbonyl group is hydrogenated by using R–Ni or Pd–C.[10] The difference is attributed to the affinity of the catalysts for phenyl group vs. heteroatoms: platinum has affinity to aromatic ring,[4] and nickel shows affinity to oxygen.[16] Palladium is known to show different behavior from other platinum metals.[20] The cis/trans ratio of products obtained on hydrogenation of **9** is mainly controlled by isomerization during the hydrogenation. A part of **4a** may be postulated to form as a consequence of the preferential adsorption of the carbonyl group on the side of the ring opposite the axial 4-hydrogen (A in Scheme III) of **9**, but not in the same plane with equatorial 4-hydrogen (B). In the case when Pd–C is catalyst, **9** is adsorbed weakly at both carbonyl and phenyl groups,[17] and the hydrogenation occurs at the carbonyl group.

Scheme III



(A) (B)

Experimental Section

The melting points and boiling points are uncorrected. The distribution of products was examined by GLC with a Shimadzu GC-8AF gas chromatograph equipped with a column (3.2-mm i.d., 1 m) containing SP-1000 on Chromosorb WAW (80–100 mesh) under 1.0 kg cm^{-2} of nitrogen, or (in the case described otherwise) with a column (3.2-mm i.d., 2 m) containing 2,4,7-trinitro-9-fluorenone (TNF, 20%) on Chromosorb WAW under 2.5 kg cm^{-2} of nitrogen. Peak areas on the chromatogram were compared to find a ratio of each component. Retention times (minutes) of the compounds obtained on the hydrogenation of **1a** are as follows at a column temperature of 220 °C: **1a**, 11.9; **2a**, 4.0; **3a**, 1.7; **4a**, 1.7; **5a**, 0.9; **6a**, 0.9; **9**, 1.4; and **10**, 0.9; and at 160 °C **3a**, 9.7; **4a**, 10.7; **5a**, 3.9; **6a**, 4.4; **7**, 0.9; **8**, 0.5; **9**, 7.4; **10**, 3.9; and biphenyl, 2.3.

Retention times (minutes) for members of the **1b** series are as follows at 165 °C: **1b**, 10.5; **2b**, 3.3; **3b**, 2.2; **4b**, 2.7; **5b**, 1.1; and **6b**, 1.3. Those of the **1c** series are as follows at 120 °C: **1c**, 12.9; and **2c**, 3.1; and with TNF at 100 °C **2c**, 12.4; **3c**, 10.1; **4c**, 10.8; **5c**, 3.1; and **6c**, 3.7. Those of the **11** series are at 150 °C: **11**, 13.5; **12**, 4.1; **13**, 3.4; **14**, 2.6; **15**, 1.4; **16**, 1.1; and 3-phenylcyclohexanone, 8.5.

General Hydrogenation Procedure. The catalysts used in these experiments were the same as those described elsewhere.[6] To the mixture of reactant (1 mmol) in EtOH (10 mL) placed in a glass autoclave R–Ni was added with EtOH (20 mL) (time 0 h). Upon substitution of air with hydrogen (4 times), the solution was stirred (700 rpm) mechanically at 50 ± 1 °C under hydrogen pressure of 5.0 kg cm^{-2}. A small amount (ca. 0.1 mL) of the mixture was taken out, filtered, and submitted to GLC after $^1/_3$, $^2/_3$, 1, 1.5, and 2 h and each hour thereafter.

Pd–C catalyst (5% palladium on carbon) was treated with hydrogen for 30 min before addition of reactant. Platinum oxide was reduced with magnetic stirring in a test tube settled in a stainless steel autoclave for 1 h.

Hydrogenation of 1a in the Presence of R–Ni. The mixture of **1a** (340 mg, 2 mmol) in EtOH (30 mL) with R–Ni (W-7, 2.0 g) was treated for 5 h. Upon filtration, the solution was evaporated, and the residue was chromatographed with hexane on silica gel (140 g). The eluate was collected in 100-mL fractions. Fractions of 300–1400 mL were a mixture of **7**, **8**, and biphenyl. Fractions of 1.4–1.7 L gave 40 mg (11%) of **2a**: mp 129–130 °C (lit.[7] mp 130–131 °C). Fractions of 1.7–2.3 L afforded 2 mg of **1a**: mp 164–165 °C (lit.[8] mp 165 °C). Fractions of 4.3–5.5 L yielded 28.5 mg (8%) of **5a**: mp 88–90 °C (lit.[10] mp 92–93 °C). Fractions of 7.1–8.0 L afforded 37 mg (11%) of **3a**: mp 74–75 °C (lit.[10] mp 76–77 °C). Fractions of 8.7–10.0 L gave 21 mg (6%) of **6a**: mp 102–104 °C (lit.[10] mp 103–104 °C). Fractions of 10.8–15.8 L afforded 118 mg (34%) of **4a**: mp 117–118 °C (lit.[10] mp 118–118.5 °C).

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Isolation of Hydrogenated Products of 1b. After treatment of the solution of **1b** in EtOAc with Pt, the resulting mixture was separated by means of column chromatography to afford **2b** mp 58–59 °C (lit.[7] mp 59 °C); **5b** $n^{25}{}_D$ 1.478 (lit.[7] 1.4797); **3b** $n^{25}{}_D$ 1.518, ^1H NMR δ 3.4 (1 H, m; lit.[24] 3.55); **6b** $n^{25}{}_D$ 1.476 (lit.[7] mp 1.477); and **4b** $n^{25}{}_D$ 1.516; ^1H NMR δ 3.0 (1 H, m; lit.[24] 3.3).

Separation of Hydrogenated Mixture of 1c. The resulting mixture was submitted on an alumina column with hexane to be seperated into a mixture of **5c** and **6c**, pure **2c**, and a mixture of **3c** and **4c**. **2c**: $n^{25}{}_D$ 1.518 (lit.[25] 1.5233); ^1H NMR δ 1.21–1.29 (1 H, m, ax-H_4), 1.31–1.45 (4 H, m), 1.71–1.73 (1 H, m, eq-H_4), 1.81–1.86 (4 H, m), 2.45 (1 H, tt, J = 3.2 and 10.8 Hz), 2.31 (3 H, s), 7.08 (4 H, s).

Each cis/trans mixture was separated by preparative HPLC using a column (20-mm i.d., 30 cm) containing Merck LiChroprep RP-18 with acetonitrile as mobile phase. **5c**: $n^{25}{}_D$ 1.476; ^1H NMR δ 0.88 (3 H, d, J = 7.0 Hz). **6c**: $n^{25}{}_D$ 1.472; ^1H NMR δ 0.83 (3 H, d, J = 6.6 Hz). **3c**: $n^{25}{}_D$ 1.515; ^1H NMR[26] δ 1.02 (3 H, d, J = 7.1 Hz). **4c**: $n^{25}{}_D$ 1.507; ^1H NMR[26] δ 0.93 (3 H, d, J = 6.6 Hz).

Isolation of the Hydrogenated Products of 11. The resulting mixture was chromatographed on silica gel with hexane to give **8**, **7**, **12** ($n^{25}{}_D$ 1.528; lit.[7] 1.5175), **16** ($n^{25}{}_D$ 1.478), **14** ($n^{25}{}_D$ 1.518), **15** ($n^{25}{}_D$ 1.480), **13** ($n^{25}{}_D$ 1.520), and 3-phenylcyclohexanone (2,4-dinitrophenylhydrazone (mp 178–180 °C, dec; lit.[27] mp 182–186 °C) in this order.

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Acid-Catalyzed Solvolysis of Highly Reactive Phosphoramidates: A Stereochemical Study

William S. Wadsworth, Jr.

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

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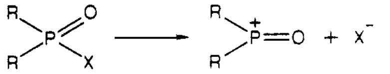
Two 2-substituted-5-(chloromethyl)-1,3,2-dioxaphosphorinanes have been prepared in which the 2-substituent is either imidazole or benzimidazole. The two phosphoramidates in which the 2-substituent is axial have opposite configurations as determined by NMR and solvolysis studies. Acid-catalyzed methanolysis in both cases is extremely rapid and proceeds by 100% inversion. However, with weak nucleophiles or a nucleophile kept in low concentration, an intermediate is formed which has enough lifetime to allow at least partial equilibration about the phosphorus atom. Although a completely free phosphacylium ion is unlikely, with aromatic solvents a similar product ratio from both isomers which may reflect a common intermediate is approached.

In the area of organophosphates and their analogues, there has been and continues to be speculation that analogous to carbon chemistry a continuum exists between dissociative and associative mechanisms. Indeed, the posibility of a process proceeding dissociatively via a phosphacylium ion analogous to an acylium ion has intrigued a number of research groups (eq 1).[1a–c] Most speculation

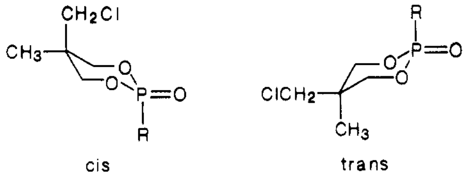


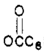
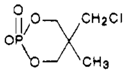
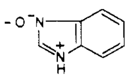
(1)

rests on kinetic data, whereas the meager stereochemical data available has led to rejection of a unimolecular dissociation leading to a discrete intermediate.[1a] If definite proof of a dissociative process based on stereochemical arguments could be illustrated, it would have implications beyond its immediate sphere for it would lend credence to the possible role of metaphosphate generated, among other ways, by the dissociation of mono- and dianions of phosphate monoesters, an area of intense study.[2a–h] This paper outlines our efforts to provide a reasonable mechanism, based on stereochemical principles, for the solvolysis of a highly reactive phosphoramidate.

The 2-substituted-5-(chloromethyl)-5-methyl-1,3,2-dioxaphosphorinane system, which we have described in a

Table I. Chemical Shifts of 2-Substituted 5-(Chloromethyl)-5-methyl-2-oxo-1,3,2-dioxaphosphorinanes[a,b]



R	CH_3	CH_2Cl	CH_3	CH_2Cl
OCH_3	0.92	3.78	1.24	3.48
$OCH(CH_3)_2$	1.00	3.80	1.20	3.55
 $O\overset{O}{\overset{\Vert}{C}}C_6H_5$	0.97	3.75	1.36	3.45
	1.03	3.77	1.41	3.42
Cl	1.10	3.90	1.40	3.46
	0.91	3.90		
OH	1.03	3.80		

[a] A number of other compounds as well as complete spectra can be found elsewhere.[3b] [b] In parts per million downfield from internal Me_4Si in $CDCl_3$.

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