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The Direct Preparation of the Esters of *p*-Nitrobenzylphosphonic Acid from *p*-Nitrobenzyl Halides*

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ABSTRACT

The reaction of sodium diisopropyl phosphite with p-nitrobenzyl bromide was studied in detail by (1) isolation and identification of all products and (2) studying the effects of radical traps, such as dicyclohexylphosphine, di-tert-butylnitroxide, and the diisopropyl phosphite anion, on product distribution. The results of the experiments carried out are compatible with a proposed X-philic substitution/SET tandem mechanism. It was demonstrated that p-nitrobenzyl chloride is also a good single-electron acceptor from the p-nitrobenzyl anion. The anion radical derived from p-nitrobenzyl chloride decomposes into the p-nitrobenzyl radical, which couples with an appropriate anion if it is present in a high enough concentration in the reaction mixture, to produce the dimer or the p-nitrobenzylphosphonate. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

One of the oldest pathways for the formation of a carbon phosphorus bond is the Michaelis–Becker reaction [1,2]. The mechanism of this reaction is assumed to be an S_N2 process involving nucleophiles of the $>P–O^-$ type. On the other hand, dialkyl phosphite anions are known to participate as single-electron donors in aromatic [3,4] as well as aliphatic [5,6] $S_{RN}1$ processes.

In the literature, one can find some examples of an unusual course of the Michaelis–Becker reaction. The reaction between bromotriphenylmethane and sodium diethyl phosphite was claimed to be a free radical process [7,8]. We have shown recently [9,10] that the anions of the $>P–O^-$ type as well as of the $>P–S^-$ type undergo a reaction with α-bromocarboxylates and -phosphonates to yield debrominated products.

Both benzylphosphonates with a wide range of substituents in the phenyl ring [11,12] and phosphonomethylpyridines [13–16] have been used in the Michaelis–Becker reaction. Exceptions are nitro derivatives; Kreutzkamp and Cordes [17] reported failures of attempted direct preparations of *p*-nitrobenzylphosphonates from *p*-nitrobenzyl chloride or bromide and trialkyl phosphites, as well as the salts of dialkyl phosphites. On the other hand, Russell et al. [18] reported that dialkyl phosphite anions react with *p*-nitrobenzyl chloride and *a,a*-dimethyl-*p*-nitrobenzyl chloride to form *p*-nitrobenzylphosphonates in a moderate to good yield and 4,4′-dinitrostilbene (in the case involving the use of *p*-nitrobenzyl chloride). The experimental data that they collected illustrate the effect of irradiation and inhibitors on the yields of these reactions. Thus, under standard conditions [20 hours of sun lamp irradiation at −78°C in tetrahydrofuran (THF)], the

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

*Reactivity of the acids of trivalent phosphorus and their derivatives. Part VII. Part VI, see Ref. [20].

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yield of the *p*-nitrobenzylphosphonate was reduced from 34% to 9% by the presence of 5 mol % of $(t\text{-Bu})_2NO^{\cdot}$. They postulated that this reaction proceeds at least partially by the free radical chain $S_{RN}1$ process.

We have shown previously [19] that *p*-nitrobenzyl chloride likewise without photostimulation in reaction with diisopropyl phosphite anion yielded diisopropyl *p*-nitrobenzylphosphonate **4** and 4,4′-dinitrostilbene **3** in almost a 1:1 ratio (3 hours; THF; 20°C). On the other hand, treatment of 1 equiv. of *p*-nitrobenzyl bromide in THF at 20°C with 1 equiv. of the diisopropyl phosphite anion, the dimethyl phosphite anion, or the dibenzylphosphinite anion produced one major product, namely, 1,2-di(*p*-nitrophenyl)ethane **6** (Scheme 1).

For several years, we have been interested in the reactivity of $>P\text{–}O^-$ nucleophiles. The results of our investigations showed [10] that, in the case of the carbon bromine bond, the bromine can be a target for nucleophilic attack by the phosphorus reagent of the $>P\text{–}O^-$ type, and also the $>P\text{–}S^-$ type, with the release of the carbanion as a nucleofuge, when it is stabilized by an electron-withdrawing substituent.

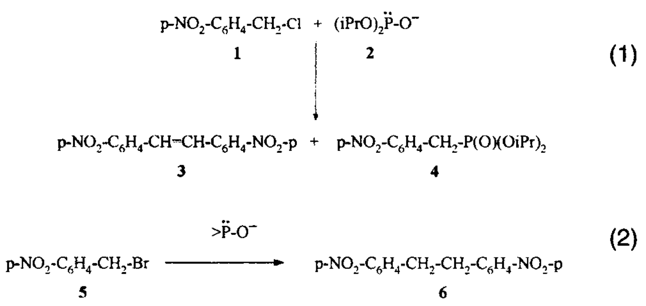
In our previous article [20], we described the reaction of *p*-substituted benzyl bromides (*p*-nitro-, *p*-cyano-, *p*-phenylsulfonyl-, *p*-carbomethoxy-, *p*-carboethoxy-, and *p*-bromo), with $>P\text{–}O^-$ ions, THF, alcohols, and toluene being the solvents. We were able to demonstrate that, according to the reduction potential of the *p*-substituted benzyl bromide, and the solvent used, formation of the P–C bond, debromination, and/or dimerization occurred. We believe the principal process in reactions of *o*- and *p*-substituted benzyl bromides (possessing electron-withdrawing groups) with the $>P\text{–}O^-$ anion systems to be X-philic substitution; the dimer is formed through a secondary process via a SET process from the carbanion to the substituted benzyl bromide (Scheme 2).

In order to check our postulate of this mechanism, we designed a new set of experiments to answer the question of what the single-electron donor is, to prove the presence of *p*-nitrobenzyl radicals in the reaction mixture and to determine whether the dimer formation is a chain process or a nonchain radical dimerization. In this article, we present the results of this investigation.

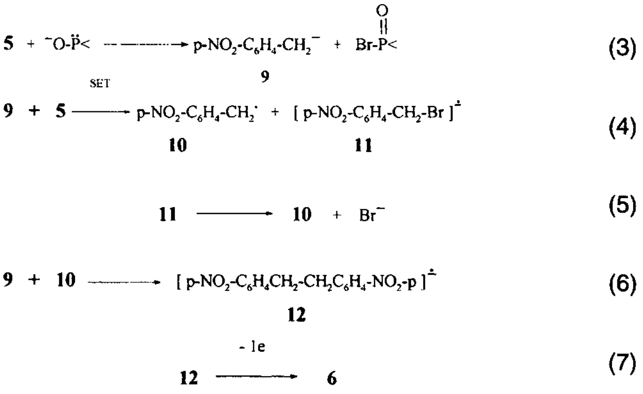
RESULTS AND DISCUSSION

Taking into consideration the isolation of *p*-nitrotoluene and methyl dibenzylphosphinate from the reaction of *p*-nitrobenzyl bromide with dibenzylphosphine oxide in methanol in the presence of sodium methoxide [20], one can conclude that a nucleophilic displacement on the bromine with release of a *p*-nitrobenzyl anion is the first step (Equation 3); such a reaction is formulated as an $S_{RN}1$ process (Scheme 2, Equations 4–7). This well-known sequence is initiated by electron transfer from the *p*-nitrobenzyl anion **9** to *p*-nitrobenzyl bromide to provide the anion radical of *p*-nitrobenzyl bromide **11**, which then fragments to produce the *p*-nitrobenzyl radical **10**. In the next step of the proposed mechanism, the *p*-nitrobenzyl anion **9** undergoes a nucleophilic addition to the *p*-nitrobenzyl radical **10** to produce the anion radical of the dimer **12** (Equation 6). Subsequent electron transfer from the dimer anion radical to *p*-nitrobenzyl bromide completes the propagation sequence (Equation 7).

The radical anions of *p*-nitrobenzyl halides **11** and *p*-nitrobenzyl radicals **10** were postulated as intermediates in the radical-nucleophilic ($S_{RN}1$) substitution reactions between anions and *p*-nitrobenzyl halides in the first publications of Kornblum et al. [21] and Russell and Danen [22], in which the $S_{RN}1$ mechanism was first proposed. Twenty years later [23,24], electron-spin-resonance spectroscopy was used to obtain confirmatory evidence for electron capture by $p\text{-}NO_2C_6H_4CH_2X$ (X = Cl, Br, No_2, N_3) to



SCHEME 1



SCHEME 2

form radical anions and dissociation of these to the *p*-nitrobenzyl radical. To find evidence supporting the presence of *p*-nitrobenzyl radicals in the reaction under investigation, we designed radical-trap experiments.

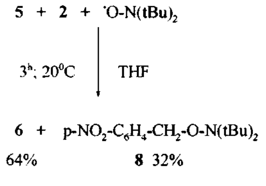
Dicyclohexylphosphine is a very weak acid and is not able to protonate >P–O⁻ nucleophiles. On the other hand, it is well known that the P–H system is a good hydrogen source for the carbon-centered radicals, and dicyclohexylphosphine has been used as a free radical trap [29]. We decided to carry out the reaction of *p*-nitrobenzyl bromide with sodium diisopropyl phosphite in THF in the presence of dicyclohexylphosphine. From this reaction, we isolated 1,2-di(*p*-nitrophenyl)ethane **6** (90%) and *p*-nitrotoluene **7** (7%), which is derived from the *p*-nitrobenzyl radical by hydrogen transfer from dicyclohexylphosphine.

The aminoxyl radical- (nitroxide) trapping technique has been successfully used to provide information about the initiation step in radical polymerization of vinyl monomers. The use of stable nitroxide radicals as traps leads to stable, nonradical adducts that can easily be manipulated and investigated by the use of a full range of spectroscopic techniques.

The aminoxyl radicals are known to be able to scavenge carbon-centered radicals at essentially diffusion-controlled rates. It has been demonstrated recently [26] that, in the presence of aminoxyl, diphenylphosphinoyl and dimethoxyphosphinoyl radicals were efficiently scavenged to produce stable phosphinic and phosphate esters, respectively. The rate of scavenging was close to that of diffusion control.

We decided to perform the reaction between *p*-nitrobenzyl bromide and sodium diisopropyl phosphite in the presence of di-*tert*-butylnitroxide, in order to obtain more information about radical intermediates of the reaction in focus (Scheme 3).

We carried out the reaction in THF (daylight; without additional illumination) of 1 equiv. of *p*-nitrobenzyl bromide with 1 equiv. of sodium diisopropyl phosphite in the presence of 1 equiv. of di-*tert*-butylnitroxide. From this reaction mixture, we isolated 1,2-di(*p*-nitrophenyl)ethane **6** (64%) and N,N-di-*tert*-butyl-O-*p*-nitrobenzylhydroxylamine **8** (32%). The O-phosphorylated N,N-di-*tert*-butylhydroxylamine was not detected. Isolation from the reaction mixture of N,N-di-*tert*-butyl-O-*p*-nitrobenzylhydroxylamine **8**, arising from coupling of di-*tert*-butylnitroxide with the *p*-nitrobenzyl radical **10**, provides strong support for the proposed mechanism (Scheme 2).



SCHEME 3

The key step in the mechanism outlined in Scheme 2 is the formation of the dimer anion radical **12** as the consequence of the reaction between the *p*-nitrobenzyl radical **10** and the *p*-nitrobenzyl anion **9** (Equation 6). The question can be asked, why, if dimer **6** is formed by coupling of the *p*-nitrobenzyl radical with *p*-nitrobenzyl anion and the subsequent one-electron oxidation, as seems likely, does this radical not couple also with a >P–O⁻ type anion to produce a *p*-nitrobenzylphosphonate by a chain mechanism?

A possible clue to the answer is that dialkyl phosphite ions [(RO)$_2$P–O⁻] are known to be radical traps in aromatic S$_{RN}$1 reactions yielding arylphosphonates [3]; also, alk-1-enyl, as well as nitroalkyl radicals, add readily to >P–O⁻ nucleophiles [25]. The reaction sequence presented in Scheme 2 appears to offer a complete answer to this question.

First, let us assume that diisopropyl bromophosphate, formed as shown in Equation 3 (X-philic substitution), is rapidly scavenged by a diisopropyl phosphite ion [27]. As a consequence, the >P–O⁻ anion would never be present in a high enough concentration to couple with the *p*-nitrobenzyl radical. When the concentration of this anion is allowed to build up sufficiently, it can compete with the *p*-nitrobenzyl anion for the *p*-nitrobenzyl radical and generate the *p*-nitrobenzylphosphonate by a chain sequence. If this scheme is correct, we would expect to find the *p*-nitrobenzylphosphonate among the products of the reaction carried out with an excess of the >P–O⁻ anion present. This expectation was verified by experimentation. We carried out the reactions of 1 equiv. of *p*-nitrobenzyl bromide with different amounts of sodium diisopropyl phosphite under standard conditions (THF; 3 hours, daylight). The results of this set of experiments are collected in Table 1.

As one can see from the data presented in Table 1, the product distribution strongly depends on the ratio of *p*-nitrobenzyl bromide to diisopropyl phosphite anion. In the case of a small concentration of diisopropyl phosphite anion in comparison with *p*-nitrobenzyl bromide (Table 1, runs 1–3), there was isolated from the reaction mixture dimer **6** and starting material **5**. The yield of dimer **6** increased with an increase in the concentration of sodium diisopro-

TABLE 1 The Products Distribution of the Reaction Between Sodium Diisopropylphosphite **2** and *p*-Nitrobenzyl Bromide **5** at Different Ratios **2**:**5**

		Isolated Yield of (%)		
Run	*Ratio **2/5***	**4**	**5**	**6**
1	0.10	—	90	8
2	0.25	—	76	22
3	0.50	—	56	42
4	1	—	18	81
5	3	23	—	74
6	10	89	—	6

TABLE 2 The Products Distribution of the Reaction among *p*-Nitrobenzyl Chloride **1**, Sodium Diisopropylphosphite **2**, and *p*-Nitrobenzyl Bromide **5** at Different Ratios of **1**:**2**:**5**

$\mathbf{1} + \mathbf{2} + \mathbf{5} \rightarrow \mathbf{3} + \mathbf{4} + \mathbf{6}$

				Isolated Yield of (%)				
Run	**1** *(mmol)*	**2** *(mmol)*	**5** *(mmol)*	**1**	**3**	**4**	**5**	**6**
1	—	2.5	2.5	—	—	—	18	81
2	1.25	2.5	1.25	18	—	—	—	79
3	2.25	5	0.25	—	7	79	—	9
4	2.5	2.5	—	50	26	21	—	—

pyl phosphite used. When the reaction of *p*-nitrobenzyl bromide was carried out with 1 equiv. of sodium diisopropyl phosphite (Table 1, run 4), one major product was produced, namely, 1,2-di(*p*-nitrophenyl)ethane **6** (81%). However, when the concentration of >P–O$^-$ anion was increased (3 equiv. of sodium diisopropyl phosphite; Table 1, run 5), there were isolated from the reaction mixture dimer **6** (74%) and the diisopropyl *p*-nitrobenzylphosphonate **4** (23%). Finally, when the reaction of *p*-nitrobenzyl bromide was carried out with 10 equiv. of sodium diisopropyl phosphite (run 6), only one major product was produced, the diisopropyl *p*-nitrobenzylphosphonate **4** (89%). The results of this set of experiments show that >P–O$^-$ anions are able to compete with *p*-nitrobenzyl anions for *p*-nitrobenzyl radicals and generate the phosphonates by a chain sequence.

We have recently demonstrated [20] another interesting feature of the reactions of *p*-substituted benzyl bromides with >P–O$^-$ anions, viz., a correlation between the reduction potentials of the benzyl bromides and the reaction course. Because of the less negative reduction potential of *p*-nitrobenzyl bromide, the electron transfer reaction is a very fast process, and the result of this is dimer **6** formation in a very high yield. On the other hand, the reduction potentials for *p*-nitrobenzyl chloride **1** and *p*-nitrobenzyl bromide **5** are -0.97 and -0.89 V (Pt/SCE, CH_3CN), respectively [28]. Since *p*-nitrobenzyl chloride and bromide have very similar reduction potentials, one can expect that they should have comparable ability to accept an electron from the *p*-nitrobenzyl anion. We decided to verify this hypothesis by experiment. The reaction of the mixture composed of *p*-nitrobenzyl chloride and bromide with sodium diisopropyl phosphite was examined. The results of this set of experiments are summarized in Table 2.

The treatment of the mixture composed of 1 equiv. of *p*-nitrobenzyl chloride **1** and 1 equiv. of *p*-nitrobenzyl bromide **5** with 2 equiv. of sodium diisopropyl phosphite (Table 2, run 2) produced one product, namely, dimer **6**, with the yield comparable to that of the reaction of *p*-nitrobenzyl bromide with diisopropyl phosphite anion (Table 2, run 1); 79% vs. 81%. In contrast to that result, treatment of the mixture composed of 0.25 equiv. of *p*-nitrobenzyl bromide **5** and 2.25 equiv. of *p*-nitrobenzyl chloride **1** with 5 equiv. of sodium diisopropyl phosphite produced diisopropyl *p*-nitrobenzylphosphonate **4** as the major product (79%) and small amounts of dimer **6** (9%) and *p,p*′-dinitrostilbene **3** (7%).

Results of experiments 2 and 3 depicted in Table 2 are in full agreement with the proposed mechanism outlined in Scheme 2. The first, and apparently the fastest, reaction is the nucleophilic attack of the >P–O$^-$ anion on the bromine atom of the *p*-nitrobenzyl bromide with the release of the *p*-nitrobenzyl anion **9**, which transfers an electron to *p*-nitrobenzyl chloride, and/or *p*-nitrobenzyl bromide, which has a similar reduction potential. Both anion radicals derived from *p*-nitrobenzyl chloride and bromide decompose into halogen anions and the *p*-nitrobenzyl radical **10**, which couples with the anion present in a high enough concentration in the reaction mixture: *p*-nitrobenzyl anion in the case of experiment 2 (Table 2) and diisopropyl phosphite anion in the case of experiment 3 (Table 2)—and generates dimer **6** or *p*-nitrobenzylphosphonate **4**, respectively, by chain sequences.

At this point, it should be pointed out that treatment of 1 equiv. of *p*-nitrobenzyl chloride with 1 equiv. of a >P–O$^-$ nucleophile produces a phosphonate and stilbene in almost equivalent molecular amounts. This means that, in contrast to the *p*-nitrobenzyl bromide case, a reaction of *p*-nitrobenzyl chloride with a >P–O$^-$ nucleophile occurs by a different mechanism. The reaction between benzyl-type chlorides and >P–O$^-$ nucleophiles is under investigation, and the results will be published subsequently.

EXPERIMENTAL

Diisopropyl phosphite was purchased from Aldrich and distilled before use. Sodium hydride (Aldrich) was washed with hexane to remove paraffin oil. Tetrahydrofuran was dried with sodium–potassium alloy. Melting points were uncorrected. The IR spectra were taken on a Jena-Zeiss IR 10 apparatus. ^{31}P NMR and ^{1}H NMR spectra were recorded with a Varian apparatus at 60, 200, or 500 MHz.

The Reaction between 4-Nitrobenzyl Bromide 5 *and the Sodium Salt of Diisopropyl Phosphite* 2 *in the Presence of DCPH in THF Solution*

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF, a solution of diisopropyl phosphite (2.5 mmol, 0.42 g) in 10 mL of THF was added. When the evolution of hydrogen had ceased, dicyclohexylphosphine (DCPH) (10 mmol, 2 g) and 4-nitrobenzyl bromide 1 (2.5 mmol, 0.54 g) in 5 mL of THF were added; the reaction mixture was stirred for 3 hours at room temperature, then diluted with 50 mL of ether, washed with NH_4Cl solution, and dried over $MgSO_4$. The solvent was removed in vacuum, and the products were separated by radial chromatography to yield: 4-nitrotoluene 7 (eluted with hexane) 0.024 g (7%), mp 52–54°C (52–54°C, Ref. [32]); IR (KBr) ν (cm^{-1}) ≡ 1520; 1355 NO_2; ^{1}H NMR ($CDCl_3$) δ = 2.46 (s, CH_3, 3H), 7.26–7.36 (m, aromatic, 2H), 8.06–8.16 (m, aromatic, 2H). 1,2-di(*p*-Nitrophenyl)ethane 6 (eluted with chloroform) 0.306 g (90%), mp 180–182°C (178–181°C, Ref. [30]); ^{1}H NMR ($CDCl_3$) δ ≡ 2.90 (s, CH_2, 4H), 6.83 (d, $^{3}J_{HH}$ = 8.00 Hz, aromatic, 4H), 7.66 (d, $^{3}J_{HH}$ = 8.00 Hz, aromatic, 4H). The products were identified by comparisons of physical data with those of authentic samples.

The Reaction between 4-Nitrobenzyl Bromide 5 *and the Sodium Salt of Diisopropyl Phosphite* 2 *in the Presence of di-t-Butyl Nitroxide in THF Solution*

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF, a solution of diisopropyl phosphite (2.5 mmol, 0.42 g) in 10 mL of THF was added. When the evolution of hydrogen had ceased, di-*t*-butyl nitroxide (2.5 mmol, 0.361 g) and 4-nitrobenzyl bromide 5 (2.5 mmol, 0.54 g) in 5 mL of THF were added. The reaction mixture was stirred for 3 hours at room temperature, diluted with 50 mL of ether, washed with NH_4Cl solution, and dried over $MgSO_4$. The solvent was removed in vacuum, and the products were separated by radial chromatography to yield: 1,2-di(*p*-nitrophenyl)ethane 6 (eluted with chloroform) 0.218 g (64%), mp 180–182°C (178–181°C, Ref. [30]); ^{1}H NMR ($CDCl_3$) δ = 2.90 (s, CH_2, 4H), 6.83 (d, $^{3}J_{HH}$ = 8.00 Hz, aromatic, 4H), 7.66 (d, $^{3}J_{HH}$ = 8.00 Hz, aromatic, 4H). N,N-di-*t*-butyl-O-(*p*-nitrobenzyl)-hydroxylamine 8 (eluted with chloroform) 0.224 g (32%), IR (film) ν (cm^{-1}) = 1210, C–O–N, 1350, 1525 NO_2; ^{1}H NMR ($CDCl_3$) δ = 1.18 (s, CH_3, 18H), 4.82 (s, CH_2–O–N<, 2H), 7.39 (d, $^{3}J_{HH}$ = 8.80 Hz, aromatic, 2H), 8.10 (d, $^{3}J_{HH}$ = 8.80 Hz, aromatic, 2H). Anal. calcd for $C_{15}H_{24}N_2O_3$: C, 64.26%; H, 8.36%; found: C, 64.34%; H, 8.21%.

The Reaction between 4-Nitrobenzyl Bromide 5 *and the Sodium Salt of Diisopropyl Phosphite* 2 *with Variable Ratios of* 2/5 *in THF Solution: General Procedure*

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF, a solution of diisopropyl phosphite (2.5 mmol, 0.42 g) in 10 mL of THF was added. When the evolution of hydrogen had ceased, 4-nitrobenzyl bromide 5 (2.5 mmol, 0.54 g) in 5 mL of THF was added, and the reaction mixture was stirred for 3 hours at room temperature, diluted with 50 mL of ether, washed with NH_4Cl solution, and dried over $MgSO_4$. The solvent was removed in vacuum, and the products were separated by radial chromatography. The products were identified by comparisons with authentic samples.

The aforementioned experiment was repeated with different ratios of 2/5. The results are summarized in Table 1, runs 1–6.

Run 5. 1,2-Di(4-nitrophenyl)ethane 6 (eluted with chloroform) 0.252 g (74%), diisopropyl 4-nitrobenzylphosphonate 4 (eluted with chloroform) 0.173 g (23%), IR (film) ν (cm^{-1}) = 1260 P=O, 1030 P–O–C, 1530, 1360 NO_2; ^{1}H NMR ($CDCl_3$) δ = 1.23 (d, $^{4}J_{PH}$ = 6.18 Hz, P–O–C–CH_3, 6H), 1.31 (d, $^{4}J_{PH}$ = 6.18 Hz, P–O–C–CH_3, 6H), 3.26 (d, $^{2}J_{PH}$ = 21.68 Hz, PCH_2, 2H), 4.55–4.70 (m, P–O–CH<, 2H), 7.08–7.18 (m, aromatic, 2H), 7.75–7.85 (m, aromatic, 2H); ^{31}P NMR ($CDCl_3$) δ = 22.61. MS exact mass calcd. for $C_{13}H_{20}NO_5P$ 301.1079; found 301.1079.

The Reaction between 4-Nitrobenzyl Bromide 5 *and 4-Nitrobenzyl Chloride* 1 *with the Sodium Salt of Diisopropyl Phosphite* 2 *in THF Solution*

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF, a solution of diisopropyl phosphite (2.5 mmol, 0.42 g) in 10 mL of THF was added. When the evolution of hydrogen had ceased, a solution of 4-nitrobenzyl bromide **5** (1.25 mmol, 0.27 g) and 4-nitrobenzyl chloride **1** (1.25 mmol, 0.214 g) in 5 mL of THF was added, and the reaction mixture was stirred for 3 hours at room temperature then diluted with 50 mL of ether, washed with NH_4Cl solution, and dried over $MgSO_4$. The solvent was removed in vacuum, and the products were separated by radial chromatography. The result is summarized in Table 2, run 2. The products were identified by comparisons with authentic samples.

To a suspension of NaH (6.0 mmol, 0.144 g) in 10 mL of THF was added diisopropyl phosphite (5.0 mmol, 0.83 g) in 10 mL of THF. When the evolution of hydrogen had ceased, a solution of 4-nitrobenzyl bromide **5** (0.25 mmol, 0.054 g) and 4-nitrobenzyl chloride **1** (2.25 mmol, 0.386 g) in 5 mL of THF was added, and the reaction mixture was stirred for 3 hours at room temperature then diluted with 50 mL of ether, washed with NH_4Cl solution, and dried over $MgSO_4$. The solvent was removed in vacuum, and the products were separated by radial chromatography. The result is summarized in Table 2, run 3. The products were identified by comparisons with authentic samples.

Run 3. 4.4′-Dinitrostilbene **3** (eluted with chloroform) 0.024 g (7%), mp 295–300°C (293°C, Ref. [31]); IR (KBr) ν (cm^{-1}) = 3050 CH=CH, 1520, 1355 NO_2; ^1H NMR ($CDCl_3$) δ = 6.70 (s, CH, 2H), 6.83 (d, $^3J_{HH}$ = 8.00 Hz, aromatic, 4H), 7.66 (d, $^3J_{HH}$ = 8.00 Hz, aromatic, 4H). 1,2-Di(4-nitrophenyl)ethane **6** (eluted with chloroform) 0.031 g (9%), diisopropyl 4-nitrobenzylphosphonate **4** (eluted with chloroform) 0.595 g (79%). The products were identified by comparisons with authentic samples.

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