$P(MeNCH_2CH_2)_3N$: A Highly Selective Reagent for Synthesizing *trans*-Epoxides from Aryl Aldehydes

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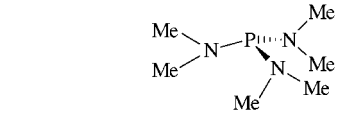
Received January 31, 2000

In contrast to its acyclic analogue $P(NMe_2)_3$ (**1**), which in benzene at room temperature reacts with two aryl aldehyde molecules bearing electron-withdrawing groups to give the corresponding diaryl epoxide as an isomeric mixture (trans/cis ratios: 72/28−51/49), $P(MeNCH_2CH_2)_3N$ (**2a**) under the same reaction conditions is found to be a highly selective reagent that provides epoxides with trans/cis ratios as high as 99/1. These reactions are faster with **2a**, because its phosphorus atom is apparently more nucleophilic than that in **1**. Thus, it is found that **2a** more easily forms 1:1 and 1:2 adducts with one or two molecules of aldehyde, respectively. These adducts apparently are intermediates in the formation of the product epoxide and the corresponding phosphine oxides of **1** and **2a**.

Introduction

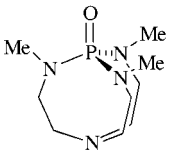
Epoxides are important starting materials in organic synthesis.[1−3] The most frequently used method to generate them is to oxidize olefins with peroxides. However, for the preparation of epoxides with sensitive structural features, this method is not always applicable.[4] For converting aryl aldehydes possessing electron-withdrawing groups to the corresponding epoxides, Mark et al. found that $P(NMe_2)_3$ (**1**) is a reagent that provides a simple and mild approach often leading to high yields of product.[4] Moreover, this transformation tolerates sensitive functional groups (such as pyridyl) that oxidative methods do not. The use of **1** has therefore constituted a practical synthetic approach.[5−8] Although *trans*-epoxides are always major products with reagent **1**, stereoselectivity is usually poor since trans/cis ratios between 2.6/1 and 1.1/1 are generally realized,[4] depending on the substrate. Thus, finding a stereoselective synthesis of epoxides from aryl aldehydes has remained challenging.

In recent years we have been exploring the chemistry of proazaphosphatranes such as **2a**−**e**,[9−14] some of which are proving to be exceedingly potent catalysts, promoters, and strong nonionic bases that facilitate a variety of useful organic transformations. For example, **2a** is an efficient catalyst for the trimerization of aryl and alkyl isocyanates that function as additives in the manufacture of Nylon-6,[15] for the protective silylation of a wide variety of sterically hindered and deactivated alcohols,[16] and for the acylation of alcohols.[17] Proazaphosphatrane **2a** is a much stronger base than DBU,[18] a commonly used nonionic base in organic synthesis. Thus, **2a** is a superior base for the synthesis of porphyrins,[19]for the dehydrohalogenation of secondary and tertiary halides,[20] and for the synthesis of a chiral fluorescence agent.[21] As a result of these and other emerging applications, **2a** has become commercially available.[22]



1

	R
2a	Me
2b	*i*-Pr
2c	Et
2d	Bn
2e	Me_3Si



3

We report herein a facile, efficient, and highly selective procedure for the synthesis of *trans*-epoxides from aryl aldehydes bearing electron-withdrawing groups. For

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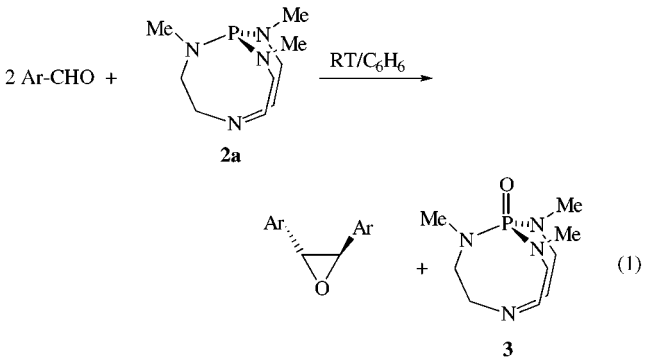
10.1021/jo000122+ CCC: $19.00
Published on Web 06/29/2000

comparison of conversions and stereoselectivity, both **1** and **2a** were used in parallel reactions. We also find that the more bulky proazaphosphatrane **2b** does not lead to epoxides, although color changes do occur.

Results and Discussion

That **2a** becomes oxidized to **3** in the reaction of two aryl aldehyde molecules in benzene to give the corresponding epoxide (eq 1) was shown by ^{31}P and ^{1}H NMR



(1)

spectroscopic analysis of a C_6D_6 solution of a 2.0/1.0 equiv ratio of **9a** to **2a** (Table 1). Only one ^{31}P resonance at 20.2 ppm corresponding to oxide **3**[10] was observed after 12 h at room temperature. In the ^{1}H NMR spectrum, the CHO proton resonance also disappeared after 12 h and a singlet at 3.95 ppm corresponding to the oxirane proton was observed (99% conversion). By comparison of ^{1}H and ^{13}C NMR spectroscopic data in the literature,[23] the epoxide **9b** present in the reaction mixture was found to be almost pure trans (trans/cis ratio = 98/2). Simply filtrering the reaction mixture and washing the filtered solid with cool benezene afforded ^{1}H NMR spectroscopically pure *trans*-**9b** in 75% yield. For comparison, the use of **1** under the same conditions led to a considerably slower reaction and lower stereoselectivity (85% conversion with a trans/cis ratio of 69/31). The isolated yield of epoxide in both bases, however, was virtually the same (74% with **1** and 75% with **2a**) because a substantial amount of starting material is converted to intermediate adducts with **2a** while no such adducts survive in the reaction with **1** (see later). The improved stereoselectivity realized with **2a** prompted us to evaluate this reagent with the substrates in Table 1. Compound **1** was used in parallel reactions to obtain conversions, yields, and trans/cis ratios for comparison with the data realized with **2a**, and these data are also included in this table.

Table 1 reveals that substrates **12a**, **13a**, and **14a** afforded no detectable or very slow reaction rates, respectively, with 0.5 equiv of **1**, although a 28% conversion to product was realized with 0.5 equiv of **2a** (trans/cis ratio = 92/8) in the case of substrate **12a**. Faster reactions were observed for substrates **4a**−**11a** with 0.5 equiv of **2a** (95−100% conversions) than those carried out with 0.5 equiv of **1** (5−95% conversions). However, the faster conversions with **2a** did not necessarily lead to higher product yields, owing to formation of comparatively robust 1:2 adducts of **2a** and the aldehyde substrate (see later), which gave rise to higher conversions of starting materials but to lower isolated yields of epoxide. Thus, for substrates **4a**, **6a**, and **7a**, compound **1** gave higher isolated yields than with **2a** although the conversions were lower.

For all the substrates tested except **13a** and **14a** (which did not react), compound **2a** gave excellent stereoselectivity (trans/cis ratios: 92/8−99/1) based on ^{1}H NMR integration of the reaction mixtures, while **1** gave isomeric mixtures (trans/cis ratios from 51/49 to 72/28) under the same conditions. The reactions were also substrate dependent: for the aryl aldehydes with electron-withdrawing groups (i.e., **4a**−**7a**), nearly quantitative conversions (>99%) were achieved within 1 h using **2a**. For the delocalized polyaromatic aldehydes (i.e., **8a**−**11a**), high conversions (95−99%) were realized within 12−14 h with **2a**. Epoxide formation was more sluggish for substrate **12a** and 60 h were necessary to obtain a 28% conversion with **2a** while less than 2% conversion was observed with **1**. However, **2a** did provide good stereoselectivity (trans/cis ratio = 92/8) despite the low conversion. In the case of ketone **13a** and **14a,** no detectable formation of corresponding epoxide **13b** and **14b** was observed even after 120 and 24 h, respectively, probably because of steric hindrance present in the substrate. Moreover, aryl aldehydes bearing electron-donating groups such as 2,5-dimethylbenzaldehyde and 2-methoxybenzaldehyde yielded no detectable epoxide formation over 2 days under the same reaction conditions. These results are consistent with earlier work[4] wherein it was shown that relatively electrophilic aldehydes promote epoxide formation. It should be noted that although the trans/cis ratios of chromatographically purified epoxides **4b**−**8b** were the same as those displayed by the corresponding reaction mixtures, we observed that when filtration was used to purify the product, higher trans/cis ratios were achieved for the isolated epoxides (**9b**−**11b**) than those observed for the corresponding reaction mixtures. Here, the *trans*-epoxides were less soluble than their cis isomers in benzene.

Two reaction pathways have been considered for **1**.[4,6] The one put forth by Mark et al. in Scheme 1[4] involves phosphorus nucleophilically attacking an aldehyde carbonyl carbon to form the 1:1 adduct **15** wherein the oxygen attacks a second molecule of the aldehyde to form the 1:2 adduct **16** (for which three resonance forms are shown). Epoxide formation would occur by carbanion attack in **16c** directly on the opposite benzyl carbon to give *trans*-epoxide or by carbanion attack on the benzylic carbon in an S_N2 manner after rotation of the O−CHAr bond to give the *cis*-epoxides. However, this mechanism was questioned by Ramirez[6] who proposed an alternative pathway (Scheme 2) wherein the phosphorus in **1** first electrophilically attacks the carbonyl oxygen of the aryl aldehyde to form a 1:1 adduct (**17**) on the grounds that the phosphorus of **1** should exhibit an even greater tendency to electrophilically attack the carbonyl oxygen than the phosphorus of trialkyl phosphites that were reported to give isolable adducts of type **18b** in Scheme 2.[6] Thus, after **17** is formed, a second molecule of the aldehyde attacks **17** to give a mixture of *erythro* (**18a**) and *threo* (**18b**) 1:2 adducts. If the *erythro* form is predominant, as might be expected for steric reasons, the *trans*-epoxide formed by loss of the oxide of **1** should predominate over the cis product. However **1** gave rise to poor stereoselectivity, with trans/cis ratios generally ranging from 1.1 to 2.6,[4] probably owing to similar steric hindrance in the *erythro* and *threo* forms of the adduct

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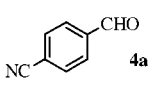
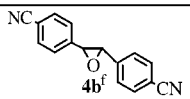
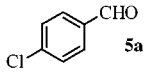
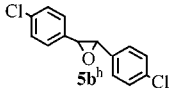
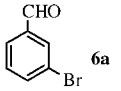
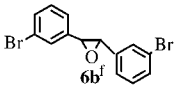
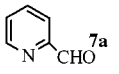
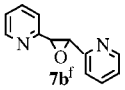
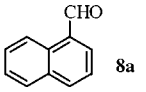
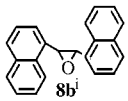
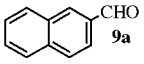
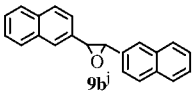
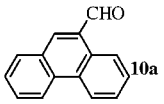
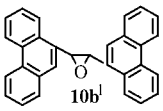
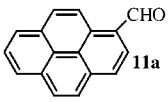
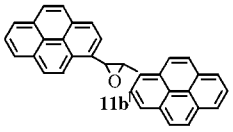
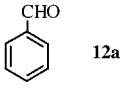
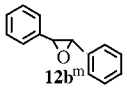
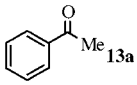
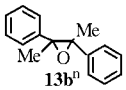
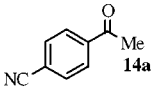
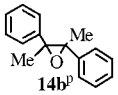
Table 1. Epoxidation of Aryl Aldehydes with 1 and 2a[a]

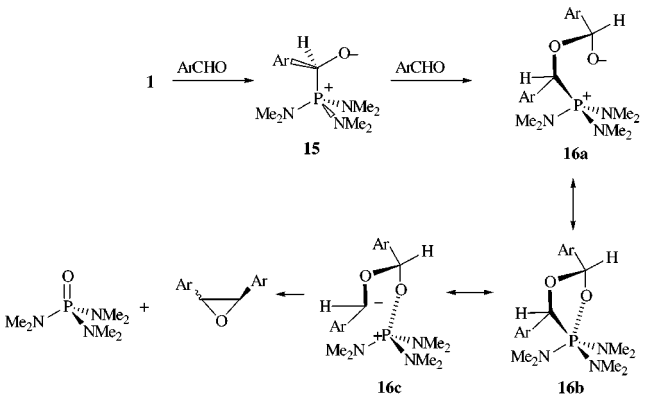
aryl aldehyde	product[b]	reaction time (h)	work-up method	%conversions[c](*trans*:*cis*)[d] yields[e](*trans*:*cis*)[d] with **2a**	with **1**
 **4a**	 **4b**[f]	0.5	col.[g] chrom.	100(98:2) 64(98:2)	95(51:49) 81(51:49)
 **5a**	 **5b**[h]	0.5	col.[g] chrom.	100(94:6) 55(95:5)	85(56:44 50(57:43)
 **6a**	 **6b**[f]	1.0	col.[g] chrom.	99(95:5) 51(96:4)	94(70:30) 69(70:30)
 **7a**	 **7b**[f]	0.5	col.[g] chrom.	100(92:8) 42(92:8)	65(63:37) 52(65:35)
 **8a**	 **8b**[i]	14	col.[g] chrom.	95(95:5) 72(99:1)	< 5(53:47) na(na)
 **9a**	 **9b**[j]	12	filtra-tion[k]	99(98:2) 75(100:0)	85(61:39 74(69:31)
 **10a**	 **10b**[l]	14	filtra-tion[k]	98(99:1) 70(100:0)	48(63:37) 37(72:28)
 **11a**	 **11b**[l]	14	filtra-tion[k]	96(99:1) 69(100:0)	73(52:48) 64(52:48)
 **12a**	 **12b**[m]	60	na	28(92:8) na (na)	< 2 (na) na (na)
 **13a**	 **13b**[n]	120	na	na[o]	na[o]
 **14a**	 **14b**[p]	24	na	na[p]	na[p]

[a] Reactions were carried out in C_6D_6 or C_6H_6 at room temperature under Ar. [b] Identification was made by comparing ^1H and ^{13}C NMR spectroscopic data with those in the references indicated. New compounds were fully characterized by ^1H and ^{13}C and HRMS (EI) spectroscopies. [c] Conversions were determined by ^1H NMR integration of signals of the methine proton in the epoxide product to the aldehyde proton in the corresponding reactant. [d] The trans:cis ratios were obtained by integrating the relevant ^1H NMR signals in the reaction mixture or of the isolated epoxide isomer mixture (see Results and Discussion). [e] Isolated yields were obtained by the indicated methods , and purity was determined by ^1H NMR spectroscopy. [f] See ref 4. [g] Silica gel column chromatography using a mixture of hexanes (95%) and ethyl acetate (5%) as the eluant. [h] Minami, T.; Matsuzaki, N.; Ohshiro, Y.; Agawa, T. *J. Chem. Soc, Perkin Trans. 1* **1980**, 1731. [i] Clark, K. B.; Bhattacharyya, K.; Das, P. K.; Scaiano, J. C.; Schaap, A. P. *J. Org. Chem.* **1992**, *57*, 3706. [j] See ref 23. [k] Since the product is insoluble in benzene, filtration followed by washing with benzene and drying in vacuo was employed to give ^1H NMR pure product. [l] See Supporting Information. [m] *Aldrich Library of ^{13}C and ^1H FT NMR spectra* **1993**, *1*(2), 222A. *Aldrich Library of ^{13}C and ^1H FT NMR spectra* **1993**, *1*(2), 221C. [n] D'Auria, M.; Mauriello, G. *Photochem. Photobiol.* **1994**, *606*, 542. [o] No observable reaction. [p] No epoxide formation was observed,

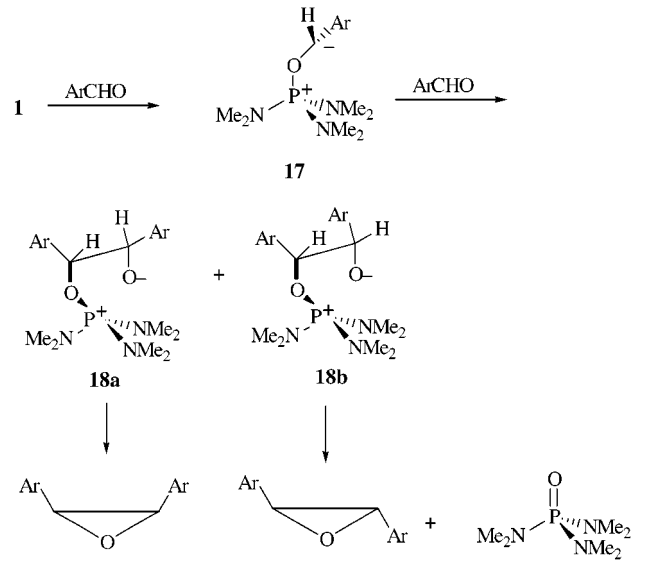
formed from a variety of substituted aryl aldehydes.[4,6] It was also reported[6] that when cyclic **19** was employed instead of **1** in the reaction with 4-nitrobenzaldehyde, the corresponding 1:2 adducts containing pentavalent phosphorus (**21a** and **21b** in Scheme 3) were isolated as a mixture in 60% yield in a 1:1 ratio.

In the present work, when 0.5 equiv of **2a** was allowed to react with **4a** in C_6D_6 at room temperature, the ^{31}P NMR spectrum of the reaction mixture exhibited three resonances (20.6, 22.7, and 22.8 ppm) in a 20:4:1 ratio. The signal at 20.6 ppm is characteristic of the oxide **3**,[10] and the other two are believed to be associated with the 1:1 and 1:2 adducts formed as intermediates. Mass spectroscopy (ESI) of the same reaction mixture revealed a large peak at 468 Da corresponding to the 1:2 adduct and a considerably smaller signal at 337 Da attributable

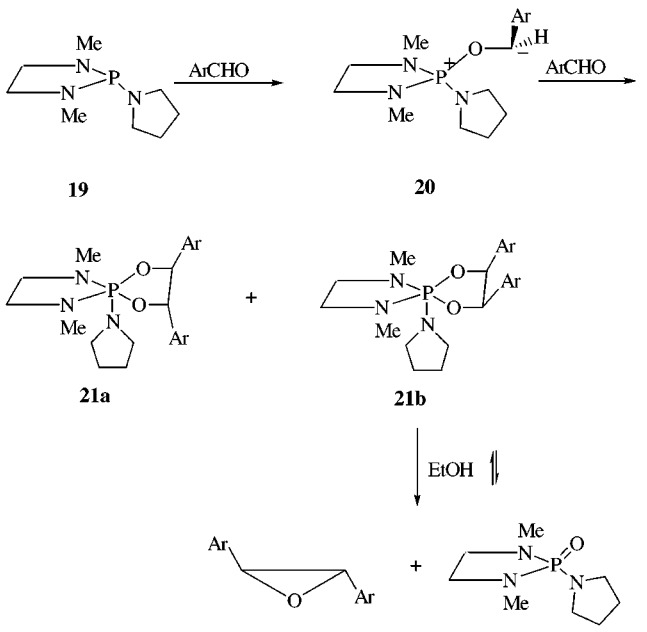
Scheme 1



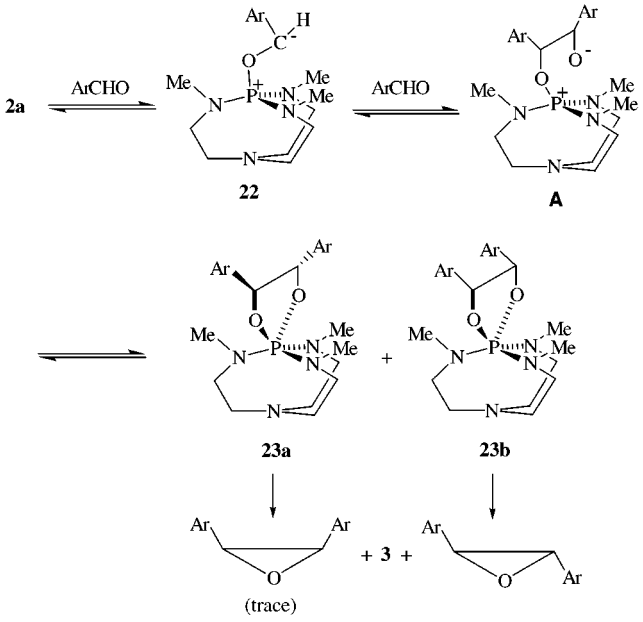
Scheme 2



Scheme 3



Scheme 4



to the 1:1 adduct. Thus, it is reasonable to assign the large ^{31}P NMR peak at 22.7 ppm to the 1:2 adduct and the smaller one at 22.8 ppm to the 1:1 adduct. The ^{1}H NMR spectrum of the reaction mixture failed to give unambiguous evidence for the ratio of these two adducts owing to peak overlaps. These observations are consistent with the reported result from the reaction of cyclic **19** in Scheme 3 with 4-nitrobenzaldehyde to give the 1:2 adduct. However, no evidence for the formation of the 1:1 adduct was reported.[6] On the basis of the ^{31}P NMR chemical shifts of the 1:1 and 1:2 adducts observed in our work (which are much closer to those of a P−O bonded adduct[24] than to that of a carbon bonded[20] adduct of **2a)** the reaction pathway proposed by Ramirez[6] (Scheme 2) seems to be supported by our results. Since **2a** like **19** is a cyclic aminophosphine, the reaction pathway in Scheme 4 is analogous to that of **19** in Scheme 3. We also note that when more bulky substrates such as **9a** were allowed to react with 0.5 equiv of **2a**, similar evidence of the presence of a mono- and diadduct was obtained from ^{31}P NMR and mass (ESI) spectroscopies. However, the ratio of **3** to 1:2 adduct to 1:1 adduct was 30:5:1, implying a higher production of **9b** from **9a** compared with the production of **4b** from **4a** (Table 1). Efforts to isolate a pure adduct of **4a** with **2a** or of **9a** with **2a** in a 1:1 or 2:1 ratio at −78 °C (in toluene) or room temperature always resulted in a mixture of **3**, the 1:2 adduct, and the 1:1 adduct. Attempts to purify the 1:1 or 1:2 adduct by recrystallization also failed.

As mentioned earlier, when the cyclic aminophosphine **19** was allowed to react with an aryl aldehyde bearing an electron-withdrawing group, a 1:2 adduct (trans:cis ratio 1:1) was isolated.[6] The cis isomer isolated from this mixture refluxing in ethanol gave the *trans*-epoxide. However, the isomeric mixture of the 1:2 adducts of **2a** observed in the present work gave no evidence of decomposition in this manner under the same conditions. During silica gel column chromatographic purification, however, these adducts did dissociate to give the starting aldehyde. Attempts to improve product yields by prolonging the reaction time, changing the reaction temperature, or using different solvents such as THF, toluene, or CH_2Cl_2 failed. By contrast, the reaction of **1** with these aldehydes provided no detectable quantities of the corresponding 1:1 or 1:2 adducts.

(24) Liu, X.; Verkade, J. G. *Inorg. Chem.* **1998**, *37*, 5189.

Although **1** reacts with 1 equiv of benzaldehyde to produce a 1:1 adduct,[4] aryl aldehydes bearing electron-withdrawing groups give epoxides as the dominant products and whose stereochemistry is only somewhat preferentially trans. On the other hand, when **19** was employed, an isomeric mixture of trans and cis (1:1), a 1:2 intermediate adduct was obtained from which the pure cis 1:2 adduct intermediate could be isolated.[6] The cis 1:2 adduct gave pure *trans*-epoxide in 86% yield but in <20% overall yield from the aldehyde.[6] It was found in the present work that **1** reacts much more slowly with aryl aldehydes bearing electron-withdrawing groups than **2a** (see Table 1). Owing to the possibility of transannular interaction from the axial nitrogen to the bridgehead phosphorus in **2a**, this base is stronger and perhaps more nucleophilic. Thus, **2a** was expected to be more reactive with an aldehyde carbonyl group than **1**, and this is reflected in Table 1. It is conceivable that in the use of acyclic **1** or cyclic **19** for epoxide formation from aldehydes, steric differences between cis and trans 1:2 adduct intermediates are relatively small, owing to P−N bond rotation of at least one phosphorus substituent, resulting in poor stereoselectivity. On the other hand, the structure of **2a** is rigid and the 1:2 adduct intermediate must adopt a less steric hindered conformation (Scheme 4). Somewhat surprisingly, the present work showed that the cis 1:2 adduct (**23b**) is apparently the more stable isomer. It is speculated that the steric hindrance between the aromatic rings in **23a** and the methyl groups in **2a** is higher than that in **23b** owing to a folding of the five-membered ring in **23b** away from the methyl group on the mirror plane to an "envelope" conformation with phosphorus in the "flap" position. The greater bulk and rigidity of the intermediate 1:2 adduct of **2a** than the analogue with **1** is thus perhaps responsible for the greater stereoselectivity of base **2a** as shown in Table 1. However, the cause for the survival of the 1:2 isomeric intermediate adduct of **2a** in refluxing ethanol remains unclear.

Interestingly, the isolated cis 1:2 adduct **21b** in Scheme 3 and the almost exclusively formed analogue **23b** in Scheme 4 give rise to *trans*-epoxide. This is best understood in terms of heterolytic cleavage of a P−O bond to form a zwitterion followed by rotation about the ArC−CAr bond and subsequent nucleophilic attack of the alkoxide oxygen on the adjacent aryl carbon in an S_N2 fashion to give the trans product. By inference the 1:2 adducts **21a** and **23a** lead to *cis*-epoxides. This conclusion coupled with the stereoselectivity for *trans*-epoxide in our reaction supports our assignment of the cis configuration to the greatly predominant 1:2 adduct isomer **23b**.

When ketone **14a** was allowed to react with **1**, no change was observed in the ^{1}H NMR spectrum of the reaction mixture. However, when **2a** was allowed to react with **14a** in a 1:2 ratio, a ^{1}H NMR spectrum of the reaction mixture showed that the decrease in intensity of the pair of aromatic proton doublets for the substrate was accompanied by the formation of two new doublets in the aromatic range. This tentatively suggests that a 1:1 adduct is formed with relative ease, but that steric hindrance inhibits the carbanion in the 1:1 adduct from nucleophilically attacking the C═O carbon of the substrate to form a 1:2 adduct. When **2a** and **14a** were mixed in a 1:1 ratio, the same new aromatic resonance for this proposed 1:1 adduct was observed. It should be mentioned that this species is probably not a 1:2 adduct since a more complex aromatic resonance in the ^{1}H NMR spectrum should then have been observed. Upon workup of the reaction by silica gel chromatography, **14a** was recovered and no **14b** was observed.

Compound **2b**, a more sterically hindered analogue of **2a**, was also allowed to react with substrates **4a**−**9a** under the same conditions as with **2a**. Surprisingly, no epoxide products were generated according to ^{1}H and ^{31}P NMR spectroscopy. Instead, a remarkable color change from colorless to dark red was observed, which may be associated with a charge-transfer complex between the aminophosphine phosphorus as the donor and the aryl aldehyde bearing an electron-withdrawing group as the acceptor as was postulated to form as an intermediate in the reaction of **1** with aryl aldehydes.[6] The failure of **2b** to facilitate epoxide formation may well be due to the steric hindrance around the phosphorus that prevents it from nucleophilically attacking the carbonyl group of a substrate, thus restricting the interaction to charge transfer.

Experimental Section

Benzene (C_6H_6 and C_6D_6), toluene, and THF were dried with sodium. CH_2Cl_2 was dried with CaH_2. All reactions were carried out under an Ar atmosphere. Chemicals employed were purchased from Aldrich Chemicals and were used without purification unless otherwise noted. Compounds **2a**[12] and **2b**[13] were prepared according to our previously published methods. NMR, MS (ESI), and HRMS (EI) spectroscopic measurements were performed in the Instrument Services Laboratory of the Chemistry Department at Iowa State University.

General Procedure for Converting Aryl Aldehydes to Epoxides with 1 or 2a. To a solution of an aryl aldehyde (2.00 mmol) in C_6D_6 (3.0 mL) at room temperature under an Ar atmosphere was slowly added a solution of **1** or **2a** (1.05 mmol) in C_6D_6 (1.5 mL). The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopies. After the reaction time stated in Table 1, an ^{1}H NMR spectrum was recorded from which the conversion and the trans/cis ratio of the product were obtained by integration. For known compounds, these spectra were also compared with those recorded in the literature. The product epoxide was then isolated and purified by silica gel column chromatography, or filtration followed by washing (see Table 1). The identities of the purified products were confirmed by ^{1}H and ^{13}C NMR spectroscopies. In the case of new compounds, HRMS (EI) data are also given (see Supporting Information).

Acknowledgment. The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this research. The authors thank Dr. Palanichamy Ilankumaran for valuable discussions.

Supporting Information Available: ^{1}H and ^{13}C NMR and HRMS (EI) spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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