syn product.[12] The larger preference for the twist-boat transition structure by the borate is related to the small size of the alkoxy substituent as compared with the alkyl substituent. In addition, the enol borate shows greater preference for planarity than the enol borinate. This is reflected by the 3.0 kcal/mol required to rotate the borate from planar to a 90° conformation at the 3-21G level, while the borinate requires only 2.0 kcal/mol. This conclusion is probably applicable to other stereoselective aldol reactions involving metal enolates, such as titanium and zirconium enolates, where the chair transition structure is favored for *Z*-enolates, but the twist-boat is favored for *E*-enolates.

Conclusion

There is a remarkable similarity of the forming CC distance in all the aldol reactions that we have studied. Dunitz–Bürgi attack angles of 101–108° are observed in both Li and BH_2 reactions.[21] The staggered conformations around the forming CC bond are also more stable than the corresponding eclipsed in spite of the long partially formed CC bond. Since both atoms forming the new bond are pyramidalized,[20a] there is no special crowding for the alkyl substituents on the reacting carbon centers in the nonchelated transition structures.

Cyclic transition structures were found for the aldol reactions involving lithium and boron enolates. The attack of carbonyl carbon on the enolate double bond deviates from the stereoelectronically preferred trajectory due to the coordination of the metal cation with oxygens in the cyclic transition structure. Secondary orbital interactions are of minor importance in controlling the geometrical features of the transition structure. For the parent reaction of boron enolate with formaldehyde, the twist-boat transition structure is 1.4 kcal/mol lower in energy than the chair. For the substituted cases, the chairlike transition structures are preferred for *Z*-enolates, while twist-boats are preferred for *E*-enolates.

Acknowledgment. We are grateful to the National Institutes of Health for financial support of this research, the Harris Corporation for a computer grant, and the National Science Foundation and San Diego Supercomputer Center for some of the computer time used for this research.

Registry No. Formaldehyde, 50-00-0; acetaldehyde, 75-07-0; acetaldehyde enolate, 557-75-5; lithium acetaldehyde enolate, 2180-63-4; boron acetaldehyde enolate, 114551-79-0; (*E*)-propionaldehyde enolate, 57642-95-2; (*Z*)-propionaldehyde enolate, 57642-96-3.

Supplementary Material Available: Energies and Cartesian coordinates of all optimized species reported in this paper (9 pages). Ordering information is given on any current masthead page.

Metal Ion Effects in Wittig Reactions: A General Hypothesis for the Mechanism of the Wittig Reaction

William J. Ward, Jr., and William E. McEwen*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

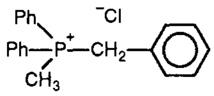
Received November 7, 1988

To evaluate better the effects of N_{2p}–P(IV) through-space interactions in Wittig reactions, a thorough study of metal ion effects in Wittig reactions lacking such interactions has been completed. As in the case of Wittig reactions with stabilized ylides, it has been determined that, with a moderated ylide, the stereochemistry (*E*:*Z* ratio) of alkene formation with an aldehyde is determined at the point that a new carbon–carbon bond has been formed to give a betaine or an oxaphosphetane intermediate. The observations that in most cases where lithium ion is present, the product mixture is enriched with the *Z* alkene, while when sodium or potassium ions are present, the *E* isomer predominates, are deemed to support the concept that a spin-paired diradical is formed as an unstable intermediate when sodium or potassium ions are present but that an ionic reaction occurs when lithium ions are present. The evidence that has been accumulated suggests that the reactions studied here (involving aromatic, heterocyclic, and aliphatic aldehydes and benzylidenediphenylmethylphosphorane or the preformed betaines, in THF at −78 °C) occur under kinetic control and without any significant degree of equilibration or Wittig reversal.

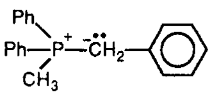
In an attempt to explore further the intricacies of the Wittig reaction, we embarked upon a detailed study of the reactions between a semistable ylide and a variety of aldehydes in the presence of lithium, sodium, or potassium ions.[1]

Results

Benzyldiphenylmethylphosphonium chloride, 1, was converted to the ylide, benzylidenediphenylmethylphosphorane, 2, by the action of an appropriate base, under anhydrous conditions and an inert atmosphere. The solvent used throughout this study was anhydrous THF. The bases used to form the ylide were *n*-butyllithium, sodium dimsyl, sodium hexamethyldisilylamide (NaHMDS), or KHMDS. The red–orange ylide solution was then cooled and caused to react with a series of aromatic aldehydes, which are displayed in the data tables. An aliphatic aldehyde, pivalaldehyde, was also employed as a comparison with the reactions involving the aromatic



1



2

---

[1] This work was presented at the Fifth International Symposium on Inorganic Ring Systems (IRIS V), University of Massachusetts, Amherst, MA, Aug 8–12, 1988; *Phosphorus Sulfur Silicon* 1989, *41*, 393.

0022-3263/90/1955-0493$02.50/0 © 1990 American Chemical Society

Table I. Wittig Reactions of Benzylidenediphenylmethylphosphorane with Aldehydes in 30 mL of THF at −78 °C (0.005-mol Scale) in the Presence of Lithium Chloride

aldehyde	yield of alkenes, %	cis/trans
C_6H_5CHO	94	66/34
p-MeC_6H_4CHO	97	67/33
p-ClC_6H_4CHO	90	54/46
p-$MeOC_6H_4CHO$	81	68/32
furfural	88	48/52
1-methylpyrrole-2-carboxaldehyde	88	74/26
pivalaldehyde	88	50/50
p-$O_2NC_6H_4CHO^b$	86	30/70
p-$CF_3C_6H_4CHO^b$	92	42/58

[a] The base used in all cases was *n*-BuLi. [b] Reaction scale 0.0025 mol, 15 mL of THF.

Table II. Wittig Reactions of Benzylidenediphenylmethylphosphorane with Aldehyde in 30 mL of THF at −78 °C (0.005-mol Scale) in the Presence of Sodium Chloride and Potassium Chloride

aldehyde	base used	yield of alkenes, %	cis/trans
C_6H_5CHO	NaDMSO[b]	98	19/81
	KHMDS[c]	96	18/82
p-MeC_6H_4CHO	NaDMSO	84	17/83
	KHMDS	96	17/83
p-ClC_6H_4CHO	NaDMSO	86	25/75
	KHMDS	88	22/78
p-$MeOC_6H_4CHO$	NaDMSO	87	18/82
	KHMDS	92	17/83
furfural	NaDMSO	82	30/70
	KHMDS	95	25/75
1-methylpyrrole-2-carboxaldehyde	NaDMSO	93	16/84
	KHMDS	99	9/91
pivalaldehyde	NaDMSO	81	23/77
	KHMDS	92	21/79
p-$O_2NC_6H_4CHO^a$	NaHMDS	80	27/73
	KHMDS	89	34/66
p-$CF_3C_6H_4CHO^a$	NaHMDS	85	25/75
	KHMDS	95	24/76

[a] Reaction scale, 0.0025 mol, 15 mL of THF. [b] Sodium dimsyl. [c] Potassium bis(trimethylsilyl)amide. [d] Sodium bis(trimethylsilyl)amide.

aldehydes. Pivalaldehyde was chosen because of its steric bulk and because it contains no acidic protons. The reaction scale was either 0.005 or 0.0025 mol, with all of the reagents being present in equivalent amounts. The product alkenes were isolated, and the cis/trans isomer ratios were determined by gas chromatography.

The effects of lithium ions on the alkene stereochemistry were studied when *n*-butyllithium was used as a base in the preparation of benzylidenediphenylmethylphosphorane, **2**; fairly high cis/trans ratios of the stilbenes were generally observed. Table I gives the reaction conditions and summarizes the data of the Wittig reactions in the presence of LiCl. The yields of the alkenes were excellent (88–97%). The amount of cis isomer was greater than or nearly equal to the amount of trans isomer in all but two cases: When the aldehydes having a strongly electron-withdrawing substituent, *p*-nitrobenzaldehyde and *p*-(trifluoromethyl)benzaldehyde, were employed, more trans alkene was produced.

When a sodium base, in this case, sodium dimsyl or sodium bis(trimethylsilyl)amide (NaHMDS), was used to prepare the ylide **2**, which was then caused to react with the various aldehydes, an inversion of the product stereochemistry was observed in most cases. In all cases, a preponderance of the trans alkene was obtained. Experimental details and results of the Wittig reactions carried out in the presence of sodium chloride are shown in Table II. The reaction yields are again excellent. In an exemplary case, the Wittig reaction involving benzaldehyde produced a cis/trans stilbene ratio of 19/81 in a combined yield of 98%. The cases involving the other aldehydes, shown in Table II, gave closely similar results.

When a potassium base (KHMDS) was utilized in preparing ylide **2**, which was then treated with the usual series of aldehydes, a preponderance of the trans alkenes was also observed. Once again, the yields were excellent. The results are also summarized in Table II. Furthermore, the cis/trans ratios of the Wittig reaction products obtained in the presence of KCl are, for the most part, nearly the same as those obtained in the presence of NaCl.

An effort was then made to compare the stereochemical results of a Wittig reaction in which metal ions were present with those when no metal halide was present in the reaction mixture. Thus, salt-free benzylidenediphenylmethylphosphorane was prepared and treated with benzaldehyde in 30 mL of THF at −78 °C. The resulting cis/trans ratio of stilbenes was 18/82, obtained in a combined yield of 95%. A comparison with the first entries of Table II indicates that NaCl and KCl provide merely spectator ions in this particular Wittig reaction, or else the salts are insoluble.

Control experiments were also performed to determine if any extraneous solvent effects (arising from the preparation or reaction of each of the various bases employed in this study) were operative. The results are as follows: The prototypical Wittig reaction between benzaldehyde and ylide **2**, NaHMDS being used as a base, resulted in a stilbene yield of 91% and a cis/trans ratio of 17/83, which is comparable to the results obtained when sodium dimsyl was employed to generate the ylide. Therefore, the presence of a small amount of DMSO or HMDS does not affect the stereochemical outcome. In another comparison, the ylide **2** was formed by the action of *n*-butyllithium on the salt **1** in 30 mL of THF, and a small amount (3 mL) of DMSO was introduced into the ylide solution before 1 equiv of benzaldehyde was added to the reaction mixture. The yield and cis/trans ratio were 90% and 22/78. When the same reaction was repeated, 1 mL of HMDS being used instead of DMSO, the yield and cis/trans ratio of stilbene were 91% and 64/36. These results indicate that the presence of a small amount of HMDS does not affect the Wittig reaction results when LiCl is the prevalent salt present. However, the results of the reaction with DMSO present mimic the salt-free case. Thus, it would appear that the DMSO effectively sequesters the lithium ion.[2] Due to the strong Lewis acid properties of Li^+ and its affinity for DMSO, this result is not unexpected.

Anion Effects in the Wittig Reaction. Bergelson et al.[3] have reported the existence of an anion effect on alkene ratios formed in some Wittig reactions. In agreement with the findings reported in this landmark paper, we have found that when benzyldiphenylmethylphosphonium iodide is treated with NaHMDS and the resulting ylide, **2**, caused to react with benzaldehyde under the usual conditions, the cis/trans ratio of stilbenes produced is 69/31, compared to a ratio of 19/81 when KHMDS is used as the base. Similar results are obtained when pivalaldehyde is used in place of benzaldehyde, as shown in Table III. Thus, the iodide anion seems to cause an inversion in the stereochemical ratio of the products when sodium ion is present, but there is little or no effect when Li^+ or K^+ is present.

---

(2) Cf.: Reitz, A. B.; Nortey, S. O.; Jordon, A. D., Jr.; Mutter, M. S.; Maryanoff, B. E. *J. Org. Chem.* **1986**, *51*, 3302.

(3) Bergelson, L. D.; Barsukov, L. I.; Shemayakin, M. M. *Tetrahedron* **1967**, *23*, 2709.

Table III. Wittig Reactions of Benzylidenediphenylmethylphosphorane with Benzaldehyde and Pivalaldehyde in 15 mL of THF at -78 °C (0.0025-mol Scale) in the Presence of Metal Iodides

aldehyde	base used	yield of alkene, %	cis/trans
benzaldehyde	*n*-BuLi	91	63/37
	NaHMDS[a]	96	69/31
	KHMDS	84	19/81
pivalaldehyde	*n*-BuLi	95	63/37
	NaHMDS	88	69/31
	KHMDS	95	21/79

[a] Sodium bis(trimethylsilyl)amide.

Table IV. Low-Temperature ^{31}P NMR Studies of the Wittig Reaction of Benzyldiphenylmethylphosphonium Chloride with *n*-Butyllithium with Subsequent Addition of Aldehydes at -78 °C in THF[a]

	^{31}P NMR,[b] ppm	
aldehyde	ylide	phosphine oxide
C_6H_5CHO	-5.3 (minor)	25.7 (major)
p-MeC_6H_4CHO	-5.3 (interm)	25.8 (major)
p-ClC_6H_4CHO	no signal	32.7
p-$MeOC_6H_4CHO$	-5.6 (major)	26.3 (interm)
furfural	-5.7 (major)	26.7 (minor)
pivalaldehyde	-5.4 (major)	26.3 (interm)

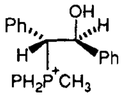
[a] See Experimental Section for essential procedure. [b] In all cases, no signal was observed for oxaphosphetane.

Table V. Low-Temperature ^{31}P NMR Studies of the Wittig Reaction of Benzyldiphenylmethylphosphonium Chloride with Sodium Bis(trimethylsilyl)amide (NaHMDS) with Subsequent Addition of Aldehydes at -78 °C in THF[a]

	^{31}P NMR, ppm		
aldehyde	ylide	phosphine oxide	oxaphosphetane
C_6H_5CHO	0.3 (minor)	25.0 (major)	no signal
p-MeC_6H_4CHO	no signal	24.9	no signal
p-ClC_6H_4CHO	0.7 (minor)	25.0 (major)	no signal
p-$MeOC_6H_4CHO$	0.9 (major)	25.0 (interm)	no signal
furfural	no signal	25.0	no signal
pivalaldehyde	0.4 (interm)	24.6 (major)	-68.7 (minor)

[a] See Experimental Section for essential procedure.

Table VI. Reaction of *erythro*-(2-Hydroxy-1,2-diphenylethyl)methyldiphenylphosphonium Iodide with Base in THF at -78 °C in the Presence of Metal Iodides

	base used	% *cis*-stilbene	yield, %
 3	*n*-BuLi	>99.9	88
	NaHMDS[a]	>99.9	97
	KHMDS	>99.9	94

[a] Sodium bis(trimethylsilyl)amide.

Table VII. Low-Temperature ^{31}P NMR Studies of the Reaction of (2-Hydroxy-1,2-diphenylethyl)methyldiphenylphosphonium Iodide with Base at -78 °C in THF in the Presence of Metal Iodide[a,b]

substrate	base used	phosphine oxide, ppm
3	*n*-BuLi	35.0[c]
3	NaHMDS	29.5[d]
3	KHMDS	26.8[d]

[a] See Experimental Section for essential details. [b] In all cases, no signal was observed for oxaphosphetane. [c] An additional, small, unknown peak was present at 50.4 ppm. No ylide signal was observed. [d] No other signals were apparent.

Investigation of Reaction Reversibility. Several methods were utilized to determine if the Wittig reactions under consideration are operating under conditions of kinetic control or thermodynamic control, the latter allowing for equilibrium between reagents and reaction intermediates. These methods included putative competition experiments,[4] low-temperature ^{31}P NMR studies,[4,5] and studies of an alternative Wittig reaction via the epoxide route.[6-8]

Competition experiments were attempted in which furfural or *p*-chlorobenzaldehyde was added to the usual ylide **2** at -78 °C. Shortly after this addition, 1 equiv of a second aldehyde was added to the reaction mixture. The amount of crossover product detected was negligible in each case. This is the anticipated result when rapid oxaphosphetane decomposition occurs.

Examination of the reaction solution contained in an NMR tube by means of ^{31}P NMR spectroscopy at -78 °C gave results that indicate the reactions occur under kinetic control.[9] The usual ylide, **2**, was formed from the phosphonium chloride in an NMR tube by using *n*-butyllithium or NaHMDS as a base. The desired aldehyde was then introduced into the NMR tube, and the spectrum acquired immediately thereafter. The results of the ^{31}P NMR experiments with LiCl or NaCl present are shown respectively in Tables IV and V. Only signals attributable to the ylide (δ ca. +1 to -5) and to the phosphine oxide (δ ca. +24 to +32) could be detected. Only in the case of the reaction of pivalaldehyde, when NaCl was present, could a very small signal (δ -68.7) be detected in the region where an oxaphosphetane intermediate is expected. Additional investigations would have to be carried out to determine if the signal is spurious or if this is the first true example of the detection of an oxaphosphetane derived from a semistable ylide. In all the other cases shown in Tables IV and V, no oxaphosphetane signals could be detected. Thus, as in a previous study by McEwen and Cairns[9] and in other cases,[5,10] the reactions are quite fast. These reactions may or may not be reversible, but it is clear that the energy barrier for the presumed oxaphosphetane going to products is distinctly smaller than that for it to revert to reagents.

A series of experiments involving "intramolecular Wittig reactions" were utilized as a further method to determine reversibility or lack thereof in the reactions. As in the case with stabilized ylides,[11] we have found that, with our semistabilized ylide, the oxaphosphetane stereochemistry is "locked" in once it forms. Therefore, the alkene isomer ratio is determined once the new carbon-carbon bond has been created. Specifically, *erythro*-(2-hydroxy-1,2-diphenylethyl)methyldiphenylphosphonium iodide (**3**) was synthesized by the method of Jones and Trippett.[6]

Compound **3** was then treated with *n*-butyllithium, NaHMDS, or KHMDS in anhydrous THF at -78 °C. The results are presented in Table VI. Effectively, only *cis*-

---

[4] Vedejs, E.; Snoble, K. A. J. *J. Am. Chem. Soc.* **1973**, *95*, 5778.

[5] Maryanoff, B. E.; Reitz, A. B.; Mutter, M. S.; Inners, R. R.; Almond, H. R., Jr.; Whittle, R. R.; Olofson, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 7664.

[6] Jones, E.; Trippett, S. *J. Chem. Soc. C* **1966**, 1090.

[7] Vedejs, E.; Marth, C. F.; Ruggeri, R. *J. Am. Chem. Soc.* **1988**, *110*, 3940.

[8] Vedejs, E.; Marth, C. F. *J. Am. Chem. Soc.* **1988**, *110*, 3948.

[9] McEwen, W. E.; Cairns, S. M. *Tetrahedron Lett.* **1986**, *27*, 1541.

[10] Vedejs, E.; Meier, G. P.; Snoble, K. J. *J. Am. Chem. Soc.* **1981**, *103*, 2823.

[11] Vedejs, E.; Fleck, T.; Hara, S. *J. Org. Chem.* **1987**, *52*, 4637.

Table VIII. Concentration Effect Study of Reactions of Benzylidenediphenylmethylphosphorane with Aldehydes in THF at -78 °C (0.005-mol Scale) in the Presence of Lithium Chloride

	cis/trans		
aldehyde	100 mL of THF	80 mL of THF	30 mL of THF
C_6H_5CHO	71/29	69/31	66/34
p-MeC_6H_4CHO	76/24	69/31	67/33
p-ClC_6H_4CHO	58/42	59/41	54/46
p-$MeOC_6H_4CHO$	64/36	66/34	68/32
furfural	48/52	48/52	48/52
1-methylpyrrole-2-carboxaldehyde	71/29	73/27	74/26
pivalaldehyde	45/55	46/54	50/50

stilbene was detected. Presumably, the betaine is formed, which quickly rotates and closes to the *cis*-oxaphosphetane, which decomposes to give the cis alkene. If an appreciable amount of reversibility were operative (i.e., if the oxaphosphetane reverted to ylide and aldehyde), then some stereochemical integrity would be lost, and *trans*-stilbene should be detected. Furthermore, each reaction mixture was examined by ^{31}P NMR spectroscopy at -78 °C in anhydrous THF. The suspended β-hydroxyphosphonium iodide **3** was placed in an NMR tube and cooled to -78 °C. The base was then added, and the spectrum acquired immediately. The results displayed in Table VII reveal that no oxaphosphetane signal was detected. Only a signal corresponding to the phosphine oxide was observed.

Effects of Lithium Ion Concentration. The usual Wittig reactions were carried out using *n*-butyllithium as a base and varying the amount of solvent used in the reaction from 100 to 30 mL of THF. The results, illustrated in Table VIII, show that, when the volume of solvent is changed from 100 to 30 mL, very little or no effect is observed in the cis/trans ratio of the alkene products. The yields of alkenes in all of these reactions were excellent (85-97%).

In another experiment, the lithium ion concentration was increased by the addition of an extra equivalent of lithium chloride to the reaction mixture of the usual semistable ylide plus benzaldehyde in 30 mL of THF at -78 °C. The yield and cis/trans ratio of stilbene were 89% and 68/32. These results are comparable to those found for the case where only 1 equiv of LiCl is present in the mixture. It appears that, unlike Maryanoff's results,[2] the stereochemistry of the products is not affected by lithium ion concentration, which is not unreasonable, since Maryanoff's system is fundamentally different from ours, and furthermore his reactions were found to be reversible.

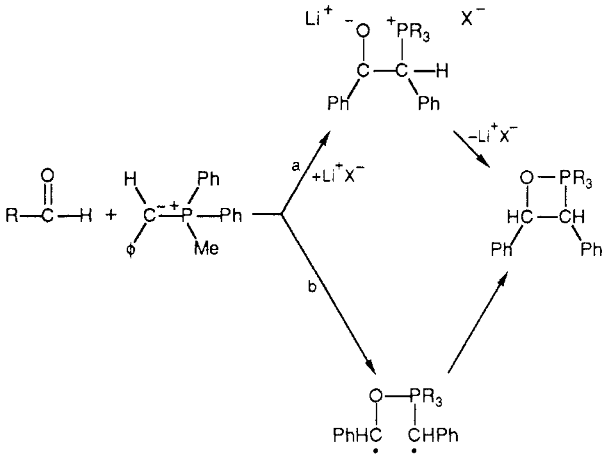
There did appear to be one case in which the lithium ion concentration had an effect on the alkene stereochemistry. As noted in Table IX, when *n*-butyllithium was employed to form the ylide, which was then treated with *p*-nitrobenzaldehyde, under the usual conditions, the cis/trans ratio of 4-nitrostilbene was 30/70. Experiments designed to increase the lithium ion concentration (by adding excess lithium chloride) in the above reaction were carried out. The results are summarized in Table IX and show that as the concentration of LiCl is increased from 1 to 3 equiv, the cis/trans ratio increases in a linear fashion.

Interpretation of Results. The results cited above, together with additional data from the literature,[12] suggest that two distinct mechanisms are operative for the Wittig reactions examined in this study. The absence or presence of a metal ion at the site of oxaphosphetane formation apparently determines the mechanistic pathway. When a metal ion is a part of the transition state leading to oxaphosphetane formation, the ionic mechanism represented in path a, Scheme I, may take place. When the reaction occurs under salt-free conditions or in the presence of nonparticipating metal salts, the spin-paired diradical mechanism shown in path b, Scheme I, is envisioned as a possibility.

Table IX. Wittig Reaction of Benzylidenediphenylmethylphosphorane with *p*-Nitrobenzaldehyde in 15 mL of THF at -78 °C (0.0025-mol Scale) in the Presence of 1-3 Equiv of LiCl

equiv of LiCl	cis/trans ratio of 4-nitrostilbenes	yield of 4-nitrostilbenes, %
1	30/70	86
2	36/64	75
3	42/58	89

Scheme I



The spin-paired diradical mechanism is of greater interest than the ionic pathway, not only because it is unique but also because it can possibly explain the heretofore most puzzling aspects of Wittig reactions, namely, why the reaction of unstable ylides with aldehydes gives mainly cis alkenes under a wide variety of conditions, why semistable ylides give variable mixtures of geometrically isomeric alkenes, and why stable ylides give mainly trans alkenes. These points will be addressed shortly.

Reaction reversal does not enter into either mechanistic picture. This conclusion is based mainly on the lack of any *trans*-stilbene produced from the deprotonation of the *erythro*-β-hydroxyphosphonium iodide **3**, which was described previously.

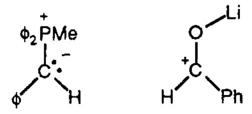
The effects of the different aldehydes on the stereochemical outcome of the Wittig reactions covered in this study will now be examined. Generally, when sodium or potassium chloride was present in the reaction solution, the presence of electron-donating or electron-withdrawing substituents in the para position of benzaldehyde had little or no effect on the overall cis/trans ratio of the alkenes produced (see Table II). The heterocyclic and aliphatic aldehydes behaved similarly. These observations are consistent with a spin-paired diradical mechanism in which the relatively nonpolar intermediate would not be affected substantially by the varying electronic effects of the aldehydes. In the lithium ion catalyzed cases, however, there are some unexplained differences in the alkene ratios derived from the various aldehydes (see Table I), especially in the cases involving the presence of electron-withdrawing groups (i.e., NO_2, CF_3), where the trans isomer predominated over the cis isomer. The explanation may be that

---

(12) McEwen, W. E.; Beaver, B. D.; Cooney, J. V. *Phosphorus Sulfur* **1985**, *25*, 255.

the presence of a strong electron-withdrawing group (in the para position), could reduce the Lewis base strength of the aldehyde carbonyl group sufficiently such that lithium ion complexation to the oxygen is greatly reduced and does not play as substantial a role in the overall reaction as with the reactions of the other, more basic, aldehydes. Thus, the diradicaloid pathway competes with the ionic one. Initially, it was believed that, in the case of 4-nitrobenzaldehyde, the lithium ion was being sequestered by the nitro group, and this may be partially correct. The addition of a second equivalent of lithium chloride to this reaction mixture did not cause the cis alkene to predominate; however, it did increase the cis/trans ratio slightly (see Table IX). Interestingly, in changing the lithium chloride concentration from 0 (extrapolated from the salt-free case) to 3 equiv (at which point the solution became saturated), a linear increase in the cis/trans ratio of 4-nitrostilbene was obtained. This result may imply that a complex equilibrium between the lithium ion and the carbonyl group, nitro group, and solvent exists. Future work is needed to quantify this concept.

Examination of the Ionic Mechanism. In the cases when the Wittig reaction is performed in the presence of lithium ion or NaI, an ionic pathway is believed to occur in the transition from reagents to products. The ionic mechanism is induced by the existence of highly polar intermediates, which are created by the complexation of the metal salts with the ylide or aldehyde, probably the latter. In the instances where lithium ion is present in the reaction mixture, the lithium ion is expected to complex the carbonyl oxygen, resulting in the polar reagent pair shown in I. Sodium (in the absence of iodide ion) and potassium ions, on the other hand, have very little Lewis acid character and would not necessarily be expected to complex with the oxygen. Thus, the carbonyl group functions in a "normal" manner; the ionic pathway is no longer favorable. Consequently, the spin-paired diradical mechanism, which depends on the presence of a strongly nucleophilic carbonyl oxygen atom, can become operative; i.e., strongly nucleophilic oxygen moieties are known to initiate attack on P(IV), forming a trigonal bipyramidal intermediate P(V) compound with the oxygen moiety occupying an apical position.



I

Molecular mechanics calculations are being carried out on the ionic reactions under consideration, and an explanation in greater depth than that provided previously[1] will be offered in a future paper for the predominant cis selectivity.

Examination of the Spin-Paired Diradical Mechanism. A closer examination of the spin-paired diradical mechanism will now be made. The consideration of this new mechanism is based in part on the arguments presented by Dewar,[13,14] who contends that cycloaddition reactions are not generally synchronous; that is, all the bond-making and bond-breaking steps do not take place simultaneously in the transition state. Dewar believes that synchronous reactions have a larger activation energy than multistep reactions, except in cases where (1) an aromatic transition state occurs, (2) when immense steric strain is relieved in the transition state, or (3) when the reaction is highly exothermic (which may possibly be applicable in the present connection).

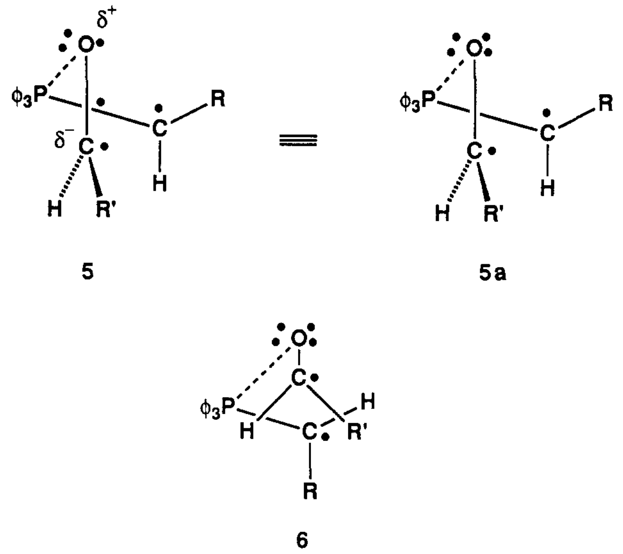


Figure 1. Spin-paired diradical intermediates based on the Vedejs model of Wittig geometry.

We have previously provided arguments,[12] including data from the literature, in support of a spin-paired diradical mechanism for the salt-free Wittig reaction. However, none of these arguments represent anything more than speculations.

Recent theoretical calculations[15] of the Wittig reaction have suggested that the formation of the new C–C bond is more advanced than the formation of the P–O bond in the transition state leading to an oxaphosphetane.[16] However, the system on which the calculations were performed is very unlike any real Wittig reaction. In fact, it is a partially mythical reaction that the theoreticians have evaluated (eq 1). Consequently, we believe that it is not

$$H_3P^{+}\text{–}^{-}CH_2 + H_2C{=}O \rightarrow CH_2{=}CH_2 + H_3P^{+}\text{–}O^{-} \qquad (1)$$

unreasonable to consider a more advanced formation of a P–O bond in the transition state, especially since oxygen nucleophiles are known to attack P(IV) readily.

The Vedejs model[7,8] for the geometry of the transition state, which is adapted by us to include the formation of an intermediate spin-paired diradical, is invoked to explain the Wittig reaction data under conditions wherein no metal ion is complexed to either reagent. According to our extension of Vedejs' mechanism, the aldehyde initially approaches the ylide in a crisscrossed fashion, and the two reagents undergo an initial reaction forming the P–O bond and giving rise to two carbon-centered radicaloid sites. The most favorable steric arrangements for the formation of the spin-paired diradical intermediates are illustrated in Figure 1. Unstable intermediate **5**, which shows the aldehyde approaching orthogonally and which places the R' group away from the ylide's R group, is the least sterically hindered arrangement. The other intermediate, **6**, has the aldehyde approaching the ylide in a parallel arrangement, such that the R and R' groups are in a skewed arrange-

---

[13] Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209.

[14] Dewar, M. J. S.; Pierini, A. B. *J. Am. Chem. Soc.* **1984**, *106*, 203.

[15] Volatron, F.; Eisenstein, O. *J. Am. Chem. Soc.* **1987**, *109*, 1, and other theoretical papers cited therein.

[16] This led us to propose formation of a spin-paired diradical (in the Harcourt sense[17]) by initial formation of the C–C bond in our first publication[12] invoking this concept. However, for reasons given in the present paper, we now postulate initial formation of a P–O bond.

[17] Harcourt, R. D.; Little, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 41.

ment, which minimizes steric interactions for this situation.

The unstable diradical intermediate **6** has a conformation such that when the spin-paired diradical closes to form the C–C bond, the trans oxaphosphetane is formed, which then undergoes pseudorotation and ring opening, forming the trans alkene.

In the Vedejs cycloaddition model, the unstable intermediate (**5**, Figure 1) that involves the orthogonal approach of the aldehyde to the ylide would lead to the cis oxaphosphetane. However, when the concept of the spin-paired diradical is combined with the orthogonal geometry, a more complicated situation exists. Under favorable circumstances it would be expected that rotation about the P–C or C–O bond could occur before the radicaloid centers combine to give the oxaphosphetane. Furthermore, it should be noted that the radicaloid centers of **5** have p orbitals that are orthogonal. Thus, some degree of bond reorganization would be required for **5** to undergo ring closure to form the cis oxaphosphetane.

The importance of radicaloid stability must now be discussed. As shown in **5a**, one of the radicaloid centers is adjacent to an oxygen atom. Such a radical would enjoy substantial Linnett[18-21] stabilization, in which an electron from the lone pair on the adjacent heteroatom is donated, forming a two-center three-electron bond (as shown in structure **5**). It should be noted that **5a** is drawn to exclude the Linnett representation for illustrative clarity, even though **5** is the more accurate picture. The stability of the radicaloid center (from the ylide moiety) is a crucial factor in the overall picture. If R were a simple alkyl group (derived from an unstable ylide), it would add little to the stability of this radicaloid center. Thus, the lifetime of this unstable intermediate should be fleeting, and bond reorganization followed by ring closure to the cis oxaphosphetane would be relatively fast. Accordingly, in the absence of any significant degree of Wittig reversal, the cis alkene would predominate, as is the actual case for reactions involving unstable ylides. However, if R is an aryl group (derived from a semistable ylide) a fairly stabilized benzylic radicaloid center would exist in **5**. It seems reasonable that the substantial stabilization, due to the existence of both Linnett and benzylic radicaloid centers, should increase the half-life of the unstable intermediate and allow rotation about either or both of the P–C and O–C bonds to occur during bond reorganization and ring closure. Therefore, a significant degree of isomerization to the thermodynamically favored trans oxaphosphetane should occur, which would yield a trans-enriched alkene mixture. Our experimental results are consistent with this concept. Furthermore, if R is an acyl, cyano, or similar group characteristic of stable ylides, then the corresponding radicaloid center in **5** would be even more stabilized, resulting in an even greater half-life. This situation would allow for maximum bond rotation and almost complete isomerization to the trans oxaphosphetane, giving the trans alkene, which is experimentally consistent for Wittig reactions involving stable ylides.

It should be kept in mind that the spin-paired diradical mechanism that we have proposed can compete with the ionic mechanism even when lithium ion or NaI is present in the reaction mixture. Not all of the Li^+ is complexed with the aldehyde or ylide; some of the Li^+ is sequestered by the solvent (THF). This is of particular importance when an electron-withdrawing substituent is present on the aldehyde. Thus, interpretations of cis/trans ratios formed in Wittig reactions involve consideration of several parameters.

It should also be mentioned that our spin-paired diradical mechanism is analogous to the mechanism proposed many years ago by Schneider,[22] at least insofar as the geometry of the formation of an unstable intermediate is concerned. However, Schneider's intermediate was a betaine, and this possibility has been refuted by the extensive ^{31}P NMR studies carried out by the Vedejs and Maryanoff groups. Also, the kinetics studies of Trippett,[6] Froyen,[23] and Schlosser[24] are inconsistent with a rate-limiting formation of a betaine in reactions carried out under lithium salt free conditions.

One of the reviewers has stated that diradicaloid pathways should be strongly influenced by adjacent groups (such as phenyl, vinyl, etc.) either in reaction rates or in side reactions. Side reactions depend on the availability of extended[17] diradicaloids, but, owing to the strong, initial dipole–dipole interaction of ylide and carbonyl compound, cyclo[17] diradicaloids would be formed in Wittig reactions.[25] Also, neither direct nor indirect rate comparisons of the systems that we have studied are readily made because all of the reactions are extremely complex, and furthermore they are apparently complete in less than 1 min at −78 °C. A full exposition of these complexities will be provided in a subsequent paper.

A kinetic isotope effect ($k_{\text{carbon-12}}/k_{\text{carbon-14}}$) at the carbonyl carbon of 1.05 has been reported for the reaction of benzophenone with isopropylidenetriphenylphosphorane in THF at 0 °C.[26a] Here, also, the relationship of this case to those of the present study is not simple, and discussion is deferred to a subsequent paper.

Experimental Section

All melting points were taken in open capillary tubes by using a Melt-Temp melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1420 ratio recording infrared spectrophotometer. ^1H NMR spectra were recorded on a Varian A-60, a Perkin-Elmer R12, or a Varian XL-200 NMR instrument. ^{31}P NMR spectra were recorded on a Varian XL-300 NMR instrument, and ^{13}C NMR spectra on a Varian XL-200 NMR instrument. Gas chromatographic analyses were performed on a Varian 1200 Aerograph instrument employing a 6-ft (3% SE-30, supelcoport) column and a FID detector. Elemental analyses were performed by the Microanalysis Laboratory of the University of Massachusetts, Amherst.

Thin-layer chromatography was conducted on Aldrich precoated silica gel or polyester plates No. 212,278-5. Silica gel used for column chromatography was 60–200 mesh and was 10% deactivated by mixing fresh silica gel with one-tenth the mass of water.

Standard procedures were employed in drying solvents. Thus, hexane was distilled from calcium hydride, and THF from sodium benzophenone ketyl. Aldehydes were distilled from anhydrous magnesium sulfate in an argon atmosphere. *n*-Butyllithium was standardized when needed by using sublimed diphenylacetic acid as an indicator. Most other reagents were purchased from the Aldrich Chemical Co. and used without further purification unless otherwise indicated.

---

(18) Firestone, R. A. *J. Chem. Soc. A* **1970**, 1570.
(19) Linnett, J. W. *J. Am. Chem. Soc.* **1981**, *83*, 2643.
(20) Firestone, R. A. *J. Org. Chem.* **1972**, *37*, 2181.
(21) Cf.: Viehe, H. G.; et al. *Tetrahedron Lett.* **1982**, *23*, 69.
(22) Schneider, W. P. *Chem. Commun.* **1969**, 785.
(23) Froyen, P. *Acta Chem. Scand.* **1972**, *26*, 2163.
(24) Schlosser, M.; Piskala, A.; Tarchini, C.; Tuang, H. B. *Chimia* **1975**, *29*, 341.
(25) Evidence of possible radical side reactions was provided by: Olah, G. A.; Krishnamurthy, V. V. *J. Am. Chem. Soc.* **1982**, *104*, 3987. However, this was an unusual Wittig reaction, and the interpretation of the results has been questioned.[26]
(26) (a) Yamataka, H.; Nagareda, K.; Takai, Y.; Sawada, M.; Hanafusa, T. *J. Org. Chem.* **1988**, *53*, 3877. (b) Cf. also: Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863 (a reference not available when we first submitted this paper).

In all experiments employing air-sensitive reagents, an inert atmosphere was maintained by back flushing the system with highly purified argon.

Gas chromatographic data were analyzed by use of the width at half-height measurement method. Identification of the compounds being eluted was accomplished by spiking the sample with known standards. In all cases, the retention times of the Wittig reaction products matched exactly those of the prepared standards. The given results in Tables I–III, VIII, and IX were corrected to take into account the difference in detection response between the cis and trans isomers.

All of the yields of products were determined by weight measurements using a Mettler PC440 electronic balance.

Preparation of Sodium Dimsyl. The method of Corey and Chaykovsky[27] was employed. The sodium dimsyl was titrated in THF with formanilide, triphenylmethane being used as the indicator.

Preparation of Salt-Free Benzylidenediphenylmethylphosphorane. The method of Vedejs et al.[10] was employed. The product consisted of yellow–orange needles, mp 122–124 °C; ^{1}H NMR (C_6D_6) δ 7.6–6.6 (m, 15 H), 2.59 (s, 1 H), 1.5 (d, 3 H).

Anal. Calcd for $C_{20}H_{19}P$: C, 82.74; H, 6.60; Cl, 0. Found: C, 81.99; H, 6.26; Cl, 0.14.

Typical Wittig Reaction between Benzyldiphenylmethylphosphonium Chloride and Aromatic Aldehydes in the Presence of the Appropriate Alkali Metal Chlorides. A 1.63-g (5 mmol) quantity of benzyldiphenylmethylphosphonium chloride was suspended in the appropriate volume of anhydrous THF in a round-bottom flask equipped with a magnetic stirring bar and an argon inlet. The appropriate base (*n*-butyllithium, sodium dimsyl, NaHMDS, or KHMDS; 1 equiv) was injected into the reaction flask. The resulting ylide mixture was allowed to stir for 0.5 h, and the reaction mixture was cooled to −78 °C by using a dry ice–acetone bath. The desired aldehyde (1 equiv) was then injected dropwise into the cooled reaction mixture and allowed to warm slowly to room temperature. After 24 h water was added to the flask, and the reaction mixture was worked up as follows: Ether was added to the product mixture, and the organic layer was separated from the aqueous layer. The aqueous layer was then washed once with ether and then with methylene chloride. The combined organic layer was dried over anhydrous magnesium sulfate, the mixture filtered, and the solvent evaporated from the filtrate. The product was then subjected to wet-column chromatography (25 g, 60–200 mesh, 10% deactivated silica gel, eluant 50/50 hexane/methylene chloride). The first fraction contained the stilbenes. The yield was obtained, and the olefin ratio determined by gas chromatography.

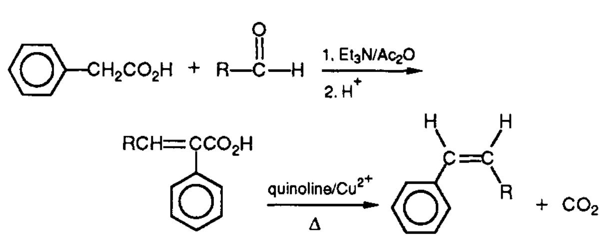
Typical Wittig Reaction between Benzyldiphenylmethylphosphonium Chloride and Aromatic Aldehydes in the Presence of Lithium or Sodium Ions with Subsequent Addition of a Crossover Aldehyde. A 1.63-g (5 mmol) quantity of benzyldiphenylmethylphosphonium chloride was suspended in 100 mL of anhydrous THF in a round-bottom flask equipped with a magnetic stirring bar and an argon inlet. Into the reaction flask was injected 1 equiv of the appropriate base (*n*-butyllithium (1.6 M), sodium dimsyl, or sodium bis(trimethylsilyl)amide (1.0 M)). The resulting red-orange solution of the ylide was stirred for 0.5 h and cooled to −78 °C (dry ice–acetone). The desired aldehyde (1 equiv) was then injected dropwise over 30 s into the cooled suspension. After 1 min, a second equivalent of the appropriate crossover aldehyde was then injected into the reaction mixture. The reaction mixture was allowed to warm slowly to room temperature and stirred for 24 h. Water was then added, and the mixture worked up by using the previously described method for Wittig reactions. An exact yield was difficult to obtain due to the separation problems of the excess aldehydes; however, the yields could be approximated and were consistent with those of the noncrossover experiments. The presence of crossover olefins was determined by gas chromatography.

Low-Temperature ^{31}P NMR Study of the Course of the Wittig Reaction. An amount of benzyldiphenylmethylphosphonium chloride equalling 0.1 g (3.1 × 10^{-4} mol) was placed in a 10-mm NMR tube which was then flushed with argon and sealed with a rubber septum. Anhydrous THF (3.5 mL) was then injected into the tube. To the suspension was added 1 equiv of the appropriate base (0.2 mL of *n*-butyllithium (1.6 M) or 0.31 mL of sodium bis(trimethylsilyl)amide (1.0 M)). The tube was then occasionally agitated for 1.5 h. The red ylide solution was cooled to −78 °C in the NMR probe and then quickly removed, and 1 equiv of aromatic aldehyde was injected into the tube by use of a syringe; the tube was quickly reinserted into the NMR probe. A spectrum was obtained immediately. The reference was an external tube containing a d_8-THF solution of triphenyl phosphate (set to −18.5 ppm).

Preparation of Benzylmethyldiphenylphosphonium Chloride. This compound was prepared by the method of Allen.[28] Colorless crystals were obtained in 77% yield, mp 242–244 °C; ^{1}H NMR ($CDCl_3$) δ 2.65 (d, 3 H), 4.95 (br d, 2 H), 7.05–8.15 (m, 15 H). These values are in good agreement with those reported in the literature.[28]

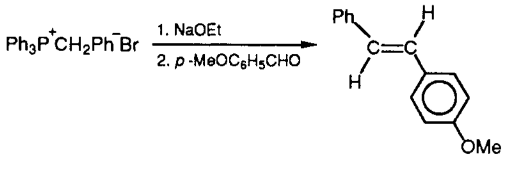
Synthetic Methods Used for the Preparation of Authentic Samples of Products. To analyze better the product alkenes from the Wittig reactions and to assign the correct structures to the compounds giving rise to the peaks in the gas chromatograph (as it turned out, all the cis alkenes displayed a shorter retention time than the trans isomers), the pure cis and pure trans alkene products were prepared separately by various synthetic routes, which will now be discussed.

The method chosen to prepare the para-substituted *cis*-stilbenes and the furyl analogue was a Perkin reaction followed by decarboxylation (eq 2). Phenylacetic acid was mixed with 4-methylbenzaldehyde, 4-chlorobenzaldehyde, 4-methoxybenzaldehyde, and furfural, respectively, in the presence of triethylamine and acetic anhydride, followed by acidification to give the corresponding α-phenylcinnamic acid derivative, which is formed preferentially in the cis configuration.[29-32] Each cinnamic acid was then purified and caused to undergo decarboxylation by heating it in the presence of quinoline and copper chromite. After workup, this procedure provided the enriched cis olefin. In the cases where R = 4-chlorophenyl and 4-methylphenyl, a small amount of the trans isomer was also isolated from the reaction mixture and used as a pure trans standard.



(2)

trans-4-Methoxystilbene was prepared by the reaction of benzyltriphenylphosphonium bromide with sodium ethoxide, with the subsequent addition of 4-methoxyaldehyde (eq 3).[33]



(3)

The syntheses of *trans*-1-(2-furyl)-2-phenylethylene and *trans*-1-(2-*N*-methylpyrryl)-2-phenylethylene were achieved by employing a Horner–Emmons reaction in each case. Thus, diethyl benzylphosphonate was treated with sodium ethoxide in DMF,

---

(27) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1345.

(28) Allen, D. W. *J. Chem. Soc.* **1970**, *13*, 1490.

(29) Buckowski, Z.; Maciaszek, S. *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **1970**, *18*, 577.

(30) Bednowitz, A. L.; Brown, R. G.; Donaruma, L. G.; Hamilton, W. C.; Kropf, R. A.; Southwick, P. L.; Stansfield, R. E. *J. Org. Chem.* **1974**, *39*, 3537.

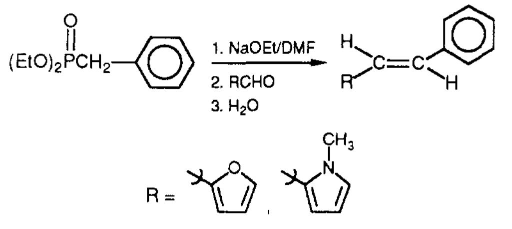
(31) Fisichella, S.; Mineri, G.; Scarlata, G.; Sciotto, D. *Tetrahedron* **1975**, *31*, 2445.

(32) Bagavant, C.; Patwardhan, B. H. *Proc. Ind. Acad. Sci. Sect. A* **1973**, *77*, 6.

(33) Friedrich, K.; Henning, H. G. *Chem. Ber.* **1959**, *92*, 2944.

with subsequent addition of furfural or *N*-methylpyrrole-2-carboxaldehyde, respectively. An aqueous workup gave the derived trans olefins in each case.

The trans isomers of 4-nitrostilbene, 4-(trifluoromethyl)stilbene, and 3,3-dimethyl-1-butenylbenzene were obtained by refluxing the appropriate cis–trans olefin mixture, obtained from the appropriate Wittig reaction (eq 4), in carbon tetrachloride containing a few crystals of iodine. After several days, the mixture was converted to >99% of the trans alkene.



(4)

When necessary, it was possible to distinguish the different geometrical isomers by the use of high-field ^{1}H NMR spectroscopy. It has been demonstrated[34] that the olefinic protons of the *cis*-stilbene produce resonances that are downfield relative to the corresponding proton of the trans isomer. Furthermore, the large coupling constants of the cis isomers are easily distinguishable from those of the trans isomer.

Physical Properties of the Alkenes. ***trans*-4-Methoxystilbene**: mp 135 °C; ^{1}H NMR ($CDCl_3$) δ 7.5–6.7 (m, 11 H), 3.75 (s, 3 H), in agreement with literature values.[33]

***cis*-4-Methoxystilbene**: bp 142 °C (3 mmHg); ^{1}H NMR ($CDCl_3$) δ 7.50–6.40 (m, 11 H), 3.50 (s, 3 H); IR (neat, cm^{-1}) 1615, 1515, 1260, 1040, 840, 700, in general agreement with literature values.[35,36]

***cis*-4-Methylstilbene**: bp 98 °C (1 mmHg); ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3 H), 6.54 (s, 2 H), 6.9–7.3 (m, 9 H), in good agreement with literature values.[37,38]

***trans*-4-Methylstilbene**: mp 116–118 °C; ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3 H), 7.08–7.55 (m, 11 H).[37,38]

***cis*-4-Chlorostilbene**: bp 98 °C (1 mmHg); ^{1}H NMR ($CDCl_3$) δ 6.48 (d, 1 H), 6.59 (d, 1 H), 7.12–7.22 (m, 9 H), in good agreement with literature values.[39]

***trans*-4-Chlorostilbene**: mp 128 °C; ^{1}H NMR ($CDCl_3$) δ 7.05 (s), 7.2–7.5 (m).[39]

***trans*-1-(2-Furyl)-2-phenylethylene**: yellow crystals, mp 53–54 °C; ^{1}H NMR ($CDCl_3$) δ 6.35–6.45 (m, 2 H), 6.98 (d, 2 H), 7.23–7.47 (m, 7 H), in agreement with literature values.[40]

***cis*-1-(2-Furyl)-2-phenylethylene**: bp 120–122 °C (8 mmHg); ^{1}H NMR ($CDCl_3$) δ 6.20 (s), 6.38 (s), 7.15–7.70 (m), in good agreement with literature values.[41]

***trans*-1-Methyl-2-styrylpyrrole**: purple plates, mp 72–74 °C (lit.[42] mp 73–75 °C); IR (melt, cm^{-1}) 1630, 1480, 960; ^{1}H NMR ($CDCl_3$) δ 3.70 (s, 3 H), 6.15 (m, 1 H), 6.5 (m, 1 H), 6.65 (m, 1 H), 6.92 (dd, 2 H), 7.15–7.50 (m, 5 H).

***cis*-1-Methyl-2-styrylpyrrole**: bp 139–155 °C (2 mmHg); IR (neat, cm^{-1}) 3010, 1630, 1480, 1305, 1090, 1060, 780, 700; ^{1}H NMR ($CDCl_3$) δ 3.48 (s), 6.00–6.10 (m), 6.40 (dd), 7.15–7.45 (m), in excellent agreement with literature values.[43]

***trans*-4-Nitrostilbene**: yellow plates, mp 158–160 °C; IR (KBr, cm^{-1}) 1585, 1505, 1335; ^{1}H NMR ($CDCl_3$) δ 7.10–7.64 (m, 9 H), 8.19–8.23 (m, 2 H), in good agreement with literature values.[44]

***trans*-4-(Trifluoromethyl)stilbene**: colorless needles, mp 134–135 °C; IR (melt, cm^{-1}) 960, 970, 1105, 1120, 1150; ^{1}H NMR ($CDCl_3$) δ 7.03–7.62 (m), in good agreement with literature values.[45,46]

Preparation of *erythro*-(2-Hydroxy-1,2-diphenylethyl)methyldiphenylphosphonium Iodide (3).[6,47,48] A colorless crystalline solid, mp 215 °C (lit.[6] mp 222–224 °C), was obtained: IR (KBr, cm^{-1}) 3260, 1430, 900; ^{1}H NMR (DMSO-d_6) δ 8.5–7.0 (m, 20 H), 6.65 (d, 1 H), 5.5–5.3 (m, 2 H), 3.4 (s, 1 H), 2.9 (d, 3 H); ^{31}P NMR (DMSO-d_6, proton decoupled) δ 25.07.

Anal. Calcd for $C_{27}H_{26}OPI$: C, 61.84; H, 5.00. Found: C, 61.65; H, 4.95.

Intramolecular Wittig Reaction Using *erythro*-(2-Hydroxy-1,2-diphenylethyl)methyldiphenylphosphonium Iodide (3) in the Presence of Lithium, Sodium, and Potassium Iodides. To a 50-mL round-bottom flask equipped with a magnetic stirrer and an argon inlet was placed 1.00 g (1.91×10^{-3} mol) of *erythro*-(2-hydroxy-1,2-diphenylethyl)methyldiphenylphosphonium iodide (**3**) in 30 mL of anhydrous THF. The mixture was cooled to −78 °C in a dry ice–acetone bath, and 1 equiv of the appropriate base (1.2 mL of *n*-butyllithium (1.6 M), 2.0 mL of sodium bis(trimethylsilyl)amide (1.0 M), or 1.4 mL of potassium bis(trimethylsilyl)amide (1.4 *M*)) was injected into the cooled suspension. The reaction mixture was allowed to warm slowly to room temperature and was stirred overnight. At the end of this time, water was added, and the reaction mixture worked up in the manner described previously for other Wittig reactions. The yields were as follows: lithium ion present, 88%; sodium ion present, 97%; potassium ion present, 94%. The reaction mixtures of all three cases were analyzed by gas chromatography, and the products were determined to be >99.9% of *cis*-stilbene.

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

---

(34) Güster, H.; Salywedel, M. *Tetrahedron* **1967**, *23*, 187.

(35) Kon, G. A. R.; Spickett, R. G. W. *J. Chem. Soc.* **1949**, 2724.

(36) *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 857.

(37) Gueston, H.; Salzwedel, M. *Tetrahedron* **1967**, *23*, 173.

(38) Wheeler, O. H.; Battle De PaBon, H. N. *J. Org. Chem.* **1965**, *30*, 1473.

(39) Schlosser, M.; Christmann, K. F. *Justus Liebigs Ann. Chem.* **1967**, *708*, 1.

(40) Seues, E. J.; Wilson, C. V. *J. Org. Chem.* **1961**, *26*, 5243.

(41) Karminski-Zamola, G.; Jakopcic, K. *J. Heterocycl. Chem.* **1981**, *18*, 193.

(42) Seues, E. J. *J. Heterocycl. Chem.* **1965**, *2*, 318.

(43) Jones, A.; Lindner, J. A. *Aust. J. Chem.* **1965**, *18*, 875.

(44) *Dictionary of Organic Compounds*, 5th ed.; Chapman and Hall: London, 1982.

(45) Wood, C. S.; Mallory, F. B. *J. Org. Chem.* **1964**, *29*, 3373.

(46) Ruasse, M. F.; Dubois, J. E. *J. Org. Chem.* **1972**, *37*, 1770.

(47) Vedejs, E.; Fuchs, P. L. *J. Am. Chem. Soc.* **1973**, *95*, 822.

(48) McEwen, W. E.; Beaver, B. D. *Phosphorus Sulfur* **1985**, *24*, 259.