Additions and Cycloadditions of 2-Phenylallylmagnesium Phenoxide to Carbon–Carbon Double Bonds

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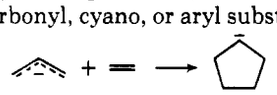
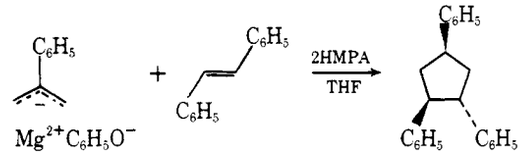
2-Phenylallylmagnesium phenoxide in tetrahydrofuran containing 2 molar equiv of hexamethylphosphoramide reacts readily with carbon–carbon double bonds which are activated by electron-withdrawing substituents. Stilbene, α-methylstyrene, β-methylstyrene, and phenanthrene give products from formal [3 + 2] cycloaddition of the allyl anion to the double bond. Acenaphthylene, α,α′-difluorostilbene, 1,1,1,4,4,4-hexafluoro-2,3-diphenyl-2-butene, and 2-[(*E*)-2-phenylethenyl]-4,4-dimethyloxazoline give adducts with formation of only one new carbon–carbon bond. 1,1-Diphenylethylene gives a cyclic adduct which is a secondary reaction product. Anthracene rapidly gives an acyclic adduct which is slowly transformed to a cyclic adduct. Attempts to determine the stereochemistry of cycloaddition of the 2-phenylallylmagnesium phenoxide to *cis*-stilbene and to *cis*-β-methylstyrene were frustrated by the rapid conversion of the olefins to their trans isomers. A stepwise carbanionic mechanism for both acyclic and cyclic additions is consistent with the results but not rigorously proven.

Cycloaddition of an allyl anion to a carbon–carbon multiple bond (eq 1) is the anionic analogue of the Diels–Alder reaction. Conservation of orbital symmetry predicts it to be a $[{}_{\pi}4_s + {}_{\pi}2_s]$ reaction in which the olefin configuration is retained in the product cyclopentyl anion.[2] Many heterocyclic analogues of the Diels–Alder reaction, 1,3-dipolar cycloadditions,[3] and also transition metal promoted [3 + 2] cycloadditions[4] are known. However, 2-phenylallyllithium, -sodium, -potassium, and -magnesium compounds,[5-8] 2-cyano-1,3-diphenylallyllithium,[9] the lithium derivative of 1,3-diphenylpropyne,[5,8] and a 2-thiomethylenecyclohexanone derivative[10] are the only formal allyl anions known to form five-membered carbocycles by intermolecular addition to carbon–carbon double bonds. Although these allyl anion cycloadditions have often been assumed to be concerted, in no case has the stereochemical course been firmly established. Kauffmann and co-workers have reported numerous cycloadditions of azaallyl anions to multiple bonds.[5] The adducts of 2-azaallyllithium with *trans*- and *cis*-stilbene appear to be those predicted by conservation of orbital symmetry.[11] Two structural features which promote anionic [3 + 2] cycloaddition are electron-withdrawing substituents on the carbon–carbon double bond and stabilization of charge in the cyclopentyl anion by a nitrogen atom (in the form of a pyrrolidine anion), or a carbonyl, cyano, or aryl substituent.



(1)

We recently reported that a variety of crown ethers, cryptands, and hexamethylphosphoramide (HMPA) catalyze cycloaddition of 2-phenylallylmagnesium phenoxide (**1**) to *trans*-stilbene to give *r*-1,*t*-2,*c*-4-triphenylcyclopentane (**2**)[8].



1 **2**

Eidenschink and Kauffmann[6] had previously obtained **2** from 2-phenylallyllithium and *trans*-stilbene but had not established its configuration. In tetrahydrofuran (THF) in the absence of complexing agents **1** does not react with *trans*-stilbene. In this paper we describe additions of **1** HMPA to a wide variety of electron-deficient carbon–carbon double bonds.

Results

2-Phenylallylmagnesium phenoxide (1) was prepared by Maercker's[12] method, cleavage of 2-phenylallyl phenyl ether (**3**) with magnesium metal in refluxing THF. The structure of **1** was confirmed by carbonation to produce 3-phenyl-3-butenoic acid (**4**), treatment with chlorotriphenyltin to produce 2-phenylallyltriphenyltin (**5**), and hydrolysis to produce α-methylstyrene and 2,5-diphenyl-1,5-hexadiene (**6**). When cleavage of **3** was attempted with lithium metal in THF only polymeric material was obtained.

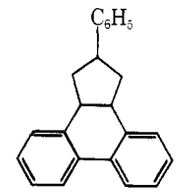
$$1 + CO_2 \rightarrow CH_2{=}C(C_6H_5)CH_2CO_2H \ (4)$$

$$1 + (C_6H_5)_3SnCl \rightarrow CH_2{=}C(C_6H_5)CH_2Sn(C_6H_5)_3 \ (5)$$

$$1 + NH_4Cl\ (aq) \rightarrow CH_2{=}C(C_6H_5)CH_3 + [CH_2{=}C(C_6H_5)CH_2]_2 \ (6)$$

Reaction of 1 HMPA with Olefins. The remarkable catalytic effect of HMPA on reaction of **1** with *trans*-stilbene prompted us to study the reactions of **1** HMPA with a variety of other olefins. The progress of each reaction was followed by GLC. The reactants and products are shown in Table I. All of the adducts were isolated by either preparative GLC or preparative liquid chromatography and characterized primarily by analyses of their mass and NMR spectra. Details are in the Experimental Section.

Reaction of phenanthrene with **1** HMPA gave the 9,10-dehydro 1:1 adduct **10**. Since **10** must be formed by dehydrogenation of the corresponding 9,10-dihydrophenanthrene (**11**), and atmospheric oxygen is known to convert dihydrophenanthrenes to phenanthrenes,[13] we attempted but failed to isolate the initial adduct **11** by carrying out all experimental

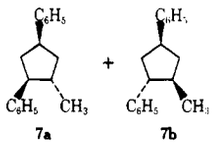
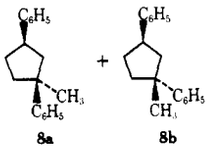
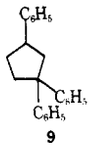
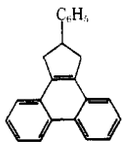
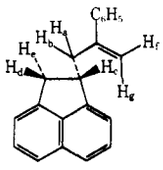
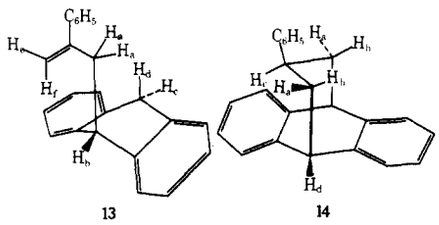
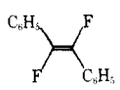
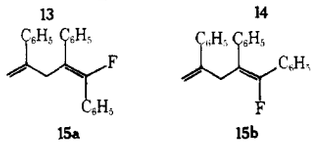
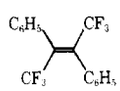
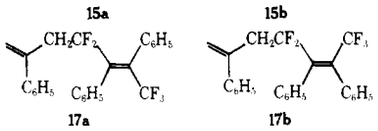


11

operations under nitrogen. Since unsubstituted 9,10-dihydrophenanthrene also was detected in the reaction mixture, **11** may have produced **10** by hydrogen transfer to phenanthrene.

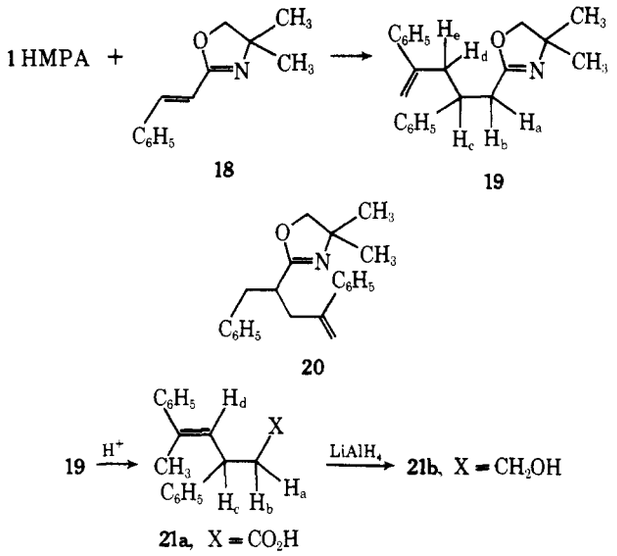
Reaction of anthracene with **1** HMPA produced acyclic adduct **13** almost immediately, but **13** disappeared and cyclic adduct **14** appeared over a period of 98 h. Bulky substituents in 9,10-dihydroanthracenes are known to prefer the less hindered axial position[14] as shown in Table I. The unusually high field resonance of H_f in **13** at δ 4.50 indicates that in the preferred conformation, H_f is deshielded by a benzene ring of the dihydroanthracene. Molecular models and the coupling

Table I. Additions of 1 HMPA to Olefins

Reactant	Product
cis- or *trans*-β-Methylstyrene	 7a + 7b
α-Methylstyrene	 8a + 8b
1,1-Diphenylethylene	 9
Phenanthrene	 10
Acenaphthylene	 12
Anthracene	 13 + 14
	 15a + 15b
 16	 17a + 17b

constants in the NMR spectrum of **14** support the conformation illustrated in Table I. The dihedral angle between H_b and H_d in a model of **14** is about 90°. Such a dihedral angle is known to minimize vicinal coupling constants. No coupling between H_b and H_d was observed. The UV spectra of **13** and **14** were nearly the same as the sums of the spectra of 9,10-dihydroanthracene and α-methylstyrene and of 9,10-dihydroanthracene and benzene, respectively.

Reaction of 1 HMPA with oxazoline **18** for 0.5 min gave the acyclic adduct (**19**) in 64% yield. Although the IR, mass, and NMR spectra all indicated a 1:1 adduct, even the 220-MHz NMR spectrum, which could be analyzed on a approximate first-order basis, did not distinguish between **19** and the isomer **20** which would result from addition of 1 HMPA to the other terminus of the carbon–carbon double bond of **18**. An attempt to distinguish **19** from **20** by NMR spectra in the presence of the paramagnetic reagent $Eu(fod)_3$ [tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedioate) europium] failed because the $Eu(fod)_3$ broadened the resonances more than it shifted them. Hydrolysis of oxazoline **19**



to carboxylic acid **21a** followed by reduction with $LiAlH_4$ gave alcohol **21b** which was identified unambiguously. The broad singlet at δ 2.5 disappeared upon addition of D_2O or $Eu(fod)_3$. Addition of increments of $Eu(fod)_3$ caused the following relative shifts: $CH_2OH > H_a$, $H_b > H_c > H_d > CH_3$. The NMR spectrum of **21a** is quite similar to that of **21b**. Although the double bond of **19** shifted from the terminal to an internal position during hydrolysis to **21a**, no breaking and making of carbon–carbon single bonds should have occurred. Therefore **19** must have the same carbon skeleton as **21b**.

Reactions of 1 HMPA with a variety of other olefins were attempted without success. The strained double bond of norbornene did not react in 4 days at room temperature. *trans*-Cyclooctene produced only a trace of *cis*-cyclooctene and no adducts in 4 days in refluxing THF. Perfluoro-2-butene reacted at 0 °C and at −78 °C to give oligomeric mixtures which contained no single product with a yield of more than 5%. No attempt was made to isolate any of the perfluoro-2-butene products.

Reactions of 1 HMPA and of 2-Phenylallylithium with *cis*- and *trans*-Stilbene. Because the rapid isomerization of *cis*- to *trans*-stilbene by 1 HMPA might lie on the same reaction path as the cycloaddition of 1 HMPA to *trans*-stilbene, we sought to learn more about the mechanism of isomerization. Even at −5 °C 1 HMPA caused complete isomerization of *cis*-stilbene (within limits of GLC detection) in 1 min. In the same time <1% of cycloadduct **2** was formed. In the absence of HMPA 2-phenylallylmagnesium phenoxide (**1**) failed to react with *trans*-stilbene in 4 days at room temperature and isomerized *cis*- to *trans*-stilbene with a half-life of about 30 h at room temperature. Two equivalents of HMPA is required to catalyze the cycloaddition; when only 1 equiv of HMPA was added, the solution of **1** did not change color and **1** failed to react with *trans*-stilbene. Isomerization of *cis*-stilbene-α,α'-d_2 by 1 HMPA at −5 °C proceeded with no loss of deuterium.

We also reinvestigated the cycloaddition of 2-phenylallyllithium to *trans*-stilbene under the conditions originally reported by Eidenschink and Kauffmann.[6] They found that a mixture of α-methylstyrene, *trans*-stilbene, and lithium diisopropylamide (LDIA) in THF gave a 41% yield of **2** in 150 h at 45 °C, but they did not establish the configuration of **2**. We verified their results and determined the configuration of **2** from its 220-MHz NMR spectrum. As we followed the reaction under their conditions by GLC–mass spectrometry, not one but four compounds appeared with molecular ions at *m/e* 298. After 166 h yields of the four fractions by GLC were 27.9, 6.2, 5.7, and 1.3%. The major isomer was **2**. The mass

spectra of the minor fractions were very similar to one another and markedly different from that of **2** and their ^1H NMR spectra indicated that they were mixtures of compounds. This suggests that most or all of the minor fractions contain acyclic isomers of **2** since there are only two other possible 1,2,4-triphenylcyclopentanes. The materials responsible for the GLC peaks corresponding to yields of 6.2 and 5.7% were isolated by preparative GLC. The complex 220-MHz NMR spectrum of each fraction appeared to be due to a mixture of two or more acyclic triphenylpentenes because of several vinyl hydrogen multiplets of nonintegral areas. Further identification was not attempted.

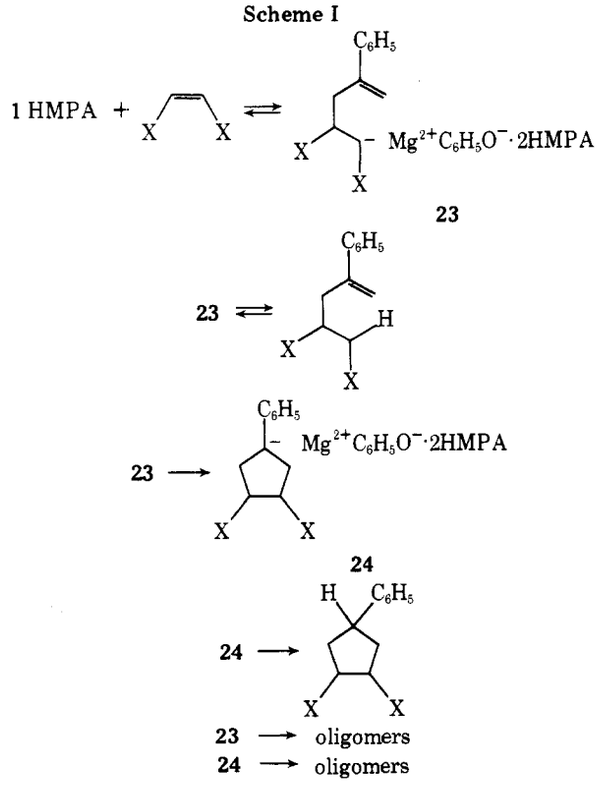
A careful examination of the reaction mixture from 1 HMPA and *trans*-stilbene by the same GLC–mass spectrometric method did not detect any of the minor isomers found in the LDIA-catalyzed reaction mixture. However, a compound was found with a molecular ion at *m/e* 416, which corresponds to a 2:1 adduct of α-methylstyrene and *trans*-stilbene. The 2:1 adduct decomposed during attempts to isolate it by preparative GLC.

When *cis*-stilbene was treated with LDIA and α-methylstyrene at 45 °C, it isomerized with a half-life of about 0.8 h. The isomerization was repeated with *cis*-stilbene-α,α'-d_2. After 4.5 h the hydrolyzed mixture contained 53% *cis*-stilbene which had lost 9% of one atom of deuterium and 47% *trans*-stilbene which had lost 50% of one atom of deuterium.

Discussion

HMPA-solvated 2-phenylallylmagnesium phenoxide in THF adds to a variety of carbon–carbon double bonds. The chief limitation is that the double bond must be substituted with at least one electron-withdrawing, carbanion-stabilizing substituent. Highly strained cycloalkenes such as norbornene and *trans*-cyclooctene do not react with 1 HMPA in refluxing THF. Several mechanisms might be invoked to explain the results, but we favor the general stepwise addition/cycloaddition mechanism in Scheme I for two reasons: (1) Scheme I can be used to explain both the cycloadducts formed from *trans*-stilbene, *trans*-β-methylstyrene, α-methylstyrene, and

Scheme I



phenanthrene, and the acyclic products formed from acenaphthylene, anthracene, α,α'-difluorostilbene, and oxazoline **18.** (2) In every reaction higher oligomers than simple 1:1 adducts were formed. Even in the cases where the major product is a 1:1 cycloadduct, there must be pathways available for stepwise addition of the intermediate cyclopentyl anion **24** or acyclic anion **23** to carbon–carbon double bonds to account for production of sizable amounts of higher molecular weight materials. We did not attempt either to trap intermediates such as **23** or **24** with alkylating or acylating agents, or to generate **23** independently and determine whether it cyclized to **24.** Successful execution of such experiments would strengthen greatly our stepwise cycloaddition interpretation, but we chose instead to explore the generality of 1 HMPA cycloadditions.

The cycloadditions could proceed by a concerted $[_\pi 4_s + _\pi 2_s]$ mechanism, but the concerted cycloaddition transition states cannot be much lower in energy than the transition states which lead to higher oligomers. In principle concerted and stepwise cycloadditions can be distinguished stereochemically. The concerted reaction must proceed with retention of the configuration of the starting olefin. Rotation about single bonds in intermediate **23** of a stepwise cycloaddition should lead to isomeric adducts which differ in configuration at the X-substituted carbon atoms. Our attempts to determine the stereochemical courses of cycloaddition of 1 HMPA to *cis*-stilbene and *cis*-β-methylstyrene were frustrated by rapid isomerization of the olefins to their more stable trans isomers under the reaction conditions.

The failure of 1 HMPA to add to norbornene and *trans*-cyclooctene does not help distinguish between concerted and stepwise cycloaddition. In the stepwise mechanism of Scheme I a carbanion-stabilizing substituent X promotes formation of intermediate **23.** In a concerted cycloaddition conjugating substituents on the $_\pi 2$ addend stabilize the transition state by making the frontier molecular orbitals of the $_\pi 2$ addend closer in energy to the frontier molecular orbitals of the 2-phenylallyl anion.[15,16] Thus an electron-rich allyl anion should add more readily to an electron-deficient phenyl-substituted double bond than to an electron-rich cycloalkene double bond regardless of the mechanism.

Cycloaddition of 1 HMPA to anthracene clearly is a stepwise process. The rapidly formed acyclic adduct **13** is slowly converted to cycloadduct **14** over a period of days.

The cycloadducts **8a** and **8b** obtained from 1 HMPA and α-methylstyrene are apparently the same as the α-methylstyrene dimer obtained much earlier by Pines and co-workers[7] by catalysis with sodium or potassium metal and alkylbenzenes at >100 °C. Our **8a** and **8b** are probably also the same compound obtained (but incorrectly assigned) from treatment of α-methylstyrene with dibenzylmagnesium.[17]

Reaction of 1 HMPA with α,α'-difluorostilbene is formally a substitution of 2-phenylallyl anion for fluoride ion at vinyl carbon. It most likely proceeds by addition of 1 HMPA to the carbon–carbon bond to form intermediate **23,** followed by loss of fluoride ion. This addition–elimination mechanism explains formation of stereoisomers **15a** and **15b** from isomerically pure α,α'-difluorostilbene.

Reaction of 1 HMPA with **16** is formally a displacement of fluoride ion by 2-phenylallyl anion at saturated carbon. An alternative electron transfer mechanism for production of **17** is (1) electron transfer from 1 HMPA to **16;** (2) loss of fluoride ion from the radical anion of **16;** (3) coupling of the 2-phenylallyl and 2,3-diphenyl-1,1,4,4,4-pentafluorobutenyl free radicals.

The isomerizations of *cis*-stilbene catalyzed by 1 HMPA and by LDIA apparently proceed by different mechanisms. The 1 HMPA process takes place without loss of deuterium

from *cis*-stilbene-α,α'-d_2 and can be explained by either reversible addition of 1 HMPA to the double bond of the stilbene as in Scheme I or reversible electron transfer from 1 HMPA to stilbene. HMPA is known to promote electron transfer reactions of organomagnesium and -lithium compounds.[18] In an electron transfer mechanism both the stilbene radical anion and the stilbene dianion formed by disproportionation of two stilbene radical anions are known to isomerize.[19] We have not attempted to detect radical anion intermediates by ESR in either the stilbene isomerizations or the cycloadditions.

Isomerization of *cis*-stilbene-α,α'-d_2 by LDIA in THF at 45 °C proceeds with partial loss of deuterium from both the *trans*-stilbene and the remaining *cis*-stilbene. This result suggests that isomerization proceeds via a vinyl carbanion intermediate. To account for the isotopically exchanged stilbenes the vinyl carbanion must abstract a proton from either THF or diisopropylamine. (LDIA and THF react slowly at room temperature to form diisopropylamine, ethylene, and the lithium enolate of acetaldehyde.)[20]

In their initial treatment of α-methylstyrene and *trans*-stilbene with LDIA to form a triphenylcyclopentane, Eidenschink and Kauffmann[6] reported a single cycloadduct of undetermined configuration. We have established that the cycloaddition proceeds stereospecifically to form **2**.[8] Because **2** is undoubtedly more stable than its isomers which have phenyl groups at C-1 and C-2 cis to one another, its exclusive formation does not distinguish between concerted and stepwise cycloadditions. Our detection of simultaneous formation of **2** and acyclic isomers from the LDIA-catalyzed reaction of α-methylstyrene and *trans*-stilbene suggests that an intermediate analogous to **23** is formed in the reaction mixture. Very likely the cycloadduct **2** is formed by the same stepwise mechanism as the acyclic adducts.

1 HMPA is not the only organomagnesium compound which adds readily to carbon–carbon double bonds. Intramolecular examples are plentiful.[21] Lehmkuhl and co-workers[22] have obtained acyclic adducts from allylmagnesium halides and a variety of olefins including norbornene, styrene, and acyclic 1-alkenes. Their experiments were carried out in diethyl ether or in hydrocarbon solvents in which the mechanism is probably a coordinative addition of the magnesium alkyl to the double bond rather than the ionic mechanism we propose for reactions of 1 HMPA. HMPA also is known to promote the 1,4 addition of ethylmagnesium bromide to 2,4,6-cyclooctatrien-1-one and the alkylmagnesium bromide initiated polymerization of α-methylstyrene.[23]

Experimental Section[24]

Temperatures are uncorrected. Preparative GLC separations were performed with a Varian A-90P chromatograph using the following columns made with copper tubing and 60/80 Chromosorb W support: A, 0.25 in. × 6 ft 10% OV-17; B, 0.25 in. × 4 ft 10% OV-17; C, 0.25 in. × 1.0 ft 8.4% SE-30. Analytical GLC was performed with a Hewlett-Packard Model 700 chromatograph equipped with a thermal conductivity detector on column D, 0.125 in. × 6 ft 10% OV-17 on 60/80 Chromosorb W in copper tubing, or with a Varian Model 2700 chromatograph equipped with flame ionization detectors using 2 mm i.d. glass columns: E, 6 ft 3% SE-30 on 100/120 Gas Chrom Q; F, 6 ft 3% OV-17 on 100/120 Gas Chrom Q. Unless otherwise noted analytical GLC runs were programmed from 75 to 290 °C at 15 °C/min with a He flow rate of 40 ml/min. *n*-Dodecane was used as the internal standard. GLC–mass spectrometry was performed on a Varian-MAT CH-7 instrument interfaced with a Varian Model 2700 gas chromatograph using column E. Medium-resolution mass spectra and deuterium analyses were performed on a Varian-MAT CH-5 instrument. Exact mass determinations of molecular ions were performed on a Varian MAT 731 instrument. ^{1}H NMR spectra were obtained with Varian A-60A, HA-100, and HR-220 spectrometers. ^{19}F NMR spectra were obtained with Varian A-56/60 and HA-100 spectrometers. Infrared spectra were obtained with a Beckman IR-12 instrument. Combustion analyses were performed by J. Nemeth and associates, University of Illinois.

Materials. THF and diethyl ether were distilled from sodium naphthalenide or sodium–benzophenone under N_2 immediately before use. Diisopropylamine, α-methylstyrene, and HMPA were distilled from CaH_2 and stored under N_2. *Caution.* Preliminary animal tests indicate that *HMPA may be carcinogenic.*[25] *n*-Butyllithium in hexane and phenyllithium in benzene/ether were obtained from Matheson Coleman and Bell or Alfa and were standardized by the 1,2-dibromoethane double titration method.[26] Magnesium turnings were washed with diethyl ether and dried under vacuum. *cis*-Stilbene[27] was vacuum distilled and found to contain 97% *cis*- and 3% *trans*-stilbene by GLC on column D. *cis*-β-Methylstyrene[28] was isolated by GLC on column B because of severe foaming encountered during attempted distillation. *trans*-Stilbene, phenanthrene, acenaphthylene, and anthracene were recrystallized. Unless noted otherwise all other materials were used as obtained from commercial sources.

Bromination of α-Methylstyrene. A mixture of 365 g of *N*-bromosuccinimide, 250 ml of α-methylstyrene, 175 ml of CCl_4, and 1.0 g of benzoyl peroxide was heated with stirring to reflux. The mixture refluxed for 15 min without additional heating. The mixture was cooled to room temperature over 3 h, filtered to remove succinimide, and partially distilled under vacuum to remove CCl_4 and excess α-methylstyrene. Vacuum distillation of the remaining material gave 258 g (74%) of mixed bromides, bp 63–72 °C (1 mm) [lit.[29] bp 56–64 °C (1 mm)]. The areas of the signals at δ 4.7 and 5.4 in the 60-MHz NMR spectrum of the mixture indicated 63% 3-bromo-2-phenylpropene and 37% 1-bromo-2-phenylpropene. *Warning: 3-Bromo-2-phenylpropene is a severe lachrymator.*

2-Phenylallyl Phenyl Ether (3). The mixed bromo-2-phenylpropenes (258 g) were treated with dry phenol and K_2CO_3 in acetone by a standard procedure.[30] Distillation gave 98% recovery of the original 1-bromo-2-phenylpropene and 157 g (91%) of **3:** bp 94–100 °C (0.02 mm); NMR ($CDCl_3$) δ 4.8 (s, 2 H), 5.4 (s, 1 H), 5.6 (s, 1 H), 6.9 (m, 3 H), 7.2 (m, 7 H); IR (neat) 3080 (m), 1620 (s), 1510 (s), 1325 (m), 1250 (s), 1190 (m), 1095 (m), 1055 (s), 1040 (s), 920 (s), 795 (m), 755 (s), 710 (s), 695 cm^{-1} (s); mass spectrum (70 eV) *m/e* (rel intensity) 210 (100), 209 (12), 195 (20), 118 (13), 117 (100), 116 (32), 115 (100), 105 (23), 94 (35), 91 (65), 77 (28).

Anal. Calcd for $C_{15}H_{14}O$: C, 85.71; H, 6.66. Found: C, 85.68; H, 6.70.

2-Phenylallylmagnesium phenoxide (1) was prepared from **3** and magnesium turnings in refluxing THF.[8,12] The preparation and all reactions of **1** were performed in an atmosphere of dry nitrogen.

3-Phenyl-3-butenoic Acid (4). Dry CO_2 was bubbled through a solution of 15 mmol of **1** in 50 ml of THF for 1.0 h. The solution was hydrolyzed with 50 ml of 2 N HCl and extracted four times with ether. The combined organic solutions were extracted three times with 50 ml of saturated aqueous Na_2CO_3. The combined aqueous solution was added slowly to 20 ml of concentrated HCl and extracted three times with ether. The ether extracts were dried and evaporated to 0.84 g (37%) of **4**, mp 40–44 °C. Recrystallization from hexane yielded 0.71 g of white crystals: mp 45–46 °C (lit.[31] mp 48–49 °C); NMR ($CDCl_3$) δ 11.4 (s, 1 H), 7.1 (m, 5 H), 5.5 (s, 1 H), 5.1 (s, 1 H), 3.2 (s, 2 H).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.21. Found: C, 74.14; H, 6.09.

2-Phenylallyltriphenyltin (5). A solution of 5.7 g of chlorotriphenyltin in 10 ml of THF was added to a solution of 15 mmol of **1** in 50 ml of THF. A white solid began to form in 15 min. The mixture was stirred overnight, hydrolyzed with 50 ml of 2 N HCl, and extracted three times with ether. The combined ether solution was dried and evaporated to a light yellow oil which was chromatographed on a 3 × 30 cm column of alumina with hexane as eluent. Evaporation of the fourth 200-ml fraction left 3.13 g (45%) of **5:** NMR ($CDCl_3$) δ 7.2 (m, 20 H), 5.0 (s, 2 H), 2.8 (s, 2 H); mass spectrum (70 eV) *m/e* (rel intensity) 468 (3.0), 467 (1.5), 466 (2.2), 465 (1.2), 404 (1.2), 356 (3.1), 355 (18.0), 354 (3.0), 353 (16.6), 352 (20.7), 351 (100.0), 350 (40.0), 349 (75.2), 348 (31.4), 347 (43.8).

General Procedure for Reactions of 1 HMPA. An equimolar amount of the reactant and 0.33 molar equiv of *n*-dodecane were added to the solution of **1** in THF in a N_2 atmosphere at room temperature. Two molar equivalents of HMPA was added with stirring. At various times 1–5-ml aliquots were withdrawn by syringe through a serum cap and rapidly added to excess dilute aqueous NH_4Cl. A few milliliters of hexane were added, and the organic phase was washed twice with 1 HCl, twice with 10% NaOH, once with 50% saturated $NaCO_3$, and once with water. The solution was dried over $MgSO_4$ and analyzed by GLC. GLC–mass spectrometry experiments were performed with the same solutions. Unless noted otherwise the samples

for NMR, IR, and elemental analysis were isolated by preparative GLC from the same solutions after evaporation of most of the solvent. Yields were determined by GLC and were not corrected by GLC response factors.

***trans*-Stilbene and 1 HMPA.** A solution of 15 mmol of 1 HMPA and 15 mmol of *trans*-stilbene was stirred for 48 h at room temperature. Periodically 5-ml aliquots of the solution were analyzed by GLC on column E. Two products were detected with molecular ions at *m/e* 298 and 416, respectively, by GLC–mass spectrometry. The former was isolated by GLC on column A at 290 °C, but the latter decomposed during attempted isolation. The compound with *m/e* 298 was identified as *r*-1,*t*-2,*c*-4-triphenylcyclopentane (**2**) by its 220-MHz NMR spectrum:[8] IR (C_2Cl_4) 3100 (m), 3080 (m), 3040 (s), 2950 (m), 1600 (s), 1500 (s), 1450 (s), 1060 (m); mass spectrum *m/e* (rel intensity) 298 (55), 207 (11), 194 (54), 193 (100), 180 (11), 179 (27), 178 (23), 168 (20), 165 (43).

Exact mass (70 eV) calcd for $C_{23}H_{22}$, 298.1723; found, 298.1722.

***cis*-Stilbene and 1 HMPA.** A reaction at room temperature conducted by the procedure used for *trans*-stilbene gave a product mixture identical with that obtained from *trans*-stilbene. The reaction was repeated by the same procedure except that the solution of 1 and *cis*-stilbene was cooled to −5 °C before addition of HMPA. GLC analysis showed the stilbene in an aliquot taken at 0.5 min to be 95% trans, and in an aliquot taken at 1.0 min to be 100% trans. In the 1.0-min aliquot the compounds of mol wt 298 and 416 were barely detectable by GLC.

***cis*-Stilbene-α,α'-d_2 and 1 HMPA.** *cis*-Stilbene-α,α'-d_2[32] was 99% cis and 1% trans by GLC and contained 98% d_2 and 2% d_1 material by mass spectrometry at low enough eV to prevent fragmentation of the molecular ions. A solution of 7.5 mmol of 1 and 15.0 mmol of HMPA in 25 ml of THF was cooled to −5 °C, and 4.5 mmol of *cis*-stilbene-α,α'-d_2 was added with stirring. After 1.0 min the entire mixture was hydrolyzed with aqueous NH_4Cl. GLC showed only α-methylstyrene and *trans*-stilbene. Both compounds were isolated and identified by mass spectrometry and NMR. By mass spectrometry at low eV the *trans*-stilbene was 98% d_2 and 2% d_1.

β-Methylstyrene and 1 HMPA. Commercial β-methylstyrene (95% trans) was dried over 3A molecular sieves. A solution of 15 mmol of β-methylstyrene and 1 HMPA in 50 ml of THF was stirred for 2.5 h at room temperature. Periodically 5.0-ml aliquots were analyzed by GLC on column E. One major product peak appeared in a maximum yield of 13% after 50 min. This material was isolated by GLC on column A at 210 °C. From the 220-MHZ NMR and mass spectra it was identified as a mixture of isomeric 1-methyl-2,4-diphenylcyclopentanes **7a** and **7b**: NMR (CCl_4) δ 1.01 (d, J = 6 Hz), 1.02 (d, J = 6 Hz), 1.35–1.6 (m), 1.75–2.8 (m), 3.2–3.4 (m), 7.14 (br s); mass spectrum *m/e* (rel intensity) 236 (87), 194 (27), 193 (41), 179 (14), 178 (10), 158 (20), 145 (20), 143 (19).

Exact mass (70 eV) calcd for $C_{18}H_{20}$, 236.1566; found, 236.1565.

When *cis*-β-methylstyrene (>99% cis) was treated in the same manner and reaction aliquots were analyzed on column F, it isomerized completely to the trans isomer in <1 min. The mixture isolated by preparative GLC had mass and 220-MHz NMR spectra identical with those obtained from the reaction of *trans*-β-methylstyrene with 1 HMPA. In the absence of HMPA under otherwise identical conditions with 1 in THF at room temperature, *cis*-β-methylstyrene underwent no isomerization in 155 h.

α-Methylstyrene and 1 HMPA. A solution of 15 mmol of α-methylstyrene and 15 mmol of 1 HMPA in 50 ml of THF was stirred for 24 h at room temperature. Periodically 5.0-ml aliquots of the solution were analyzed by GLC on column E. One major and several minor peaks were observed. The yield of the major product maximized at 35% after 3.0 h. It was isolated by GLC on column A at 280 °C and identified by 220-MHz NMR and mass spectra as a mixture of isomeric 1-methyl-1,3-diphenylcyclopentanes **8a** and **8b**: NMR (CCl_4) δ 1.36 (s, 3 H), 1.42 (s, 3 H), 1.75–2.4 (m, 11 H), 2.59 (d of d, J = 12, 8 Hz, 1 H), 3.12 (m, 1 H), 3.36 (m, 1 H), 7.0–7.4 (m, 20 H); mass spectrum *m/e* (rel intensity) 236 (37), 221 (15), 157 (12), 143 (28), 131 (16), 119 (21), 118 (100), 117 (55), 114 (24).

Exact mass calcd for $C_{18}H_{20}$, 236.1566; found, 236.1565.

1,1-Diphenylethylene and 1 HMPA. A solution of 15 mmol of 1,1-diphenylethylene and 15 mmol of 1 HMPA in 50 ml of THF was stirred for 45 h at room temperature. Periodically 5.0-ml aliquots of the solution were analyzed. GLC–mass spectrometry with column E showed four significant products with molecular ions at *m/e* 298, 368, 416, and 478. Only the first product, 1,1,3-triphenylcyclopentane (**9**), could be isolated by GLC on column B at 290 °C in sufficient quantity for identification by 220-MHz NMR spectroscopy. The complete disappearance of 1,1-diphenylethylene in <1 min and slow appearance of **9** to a yield of 28% after 45 h indicate that **9** is not a primary product of the reaction: NMR (CCl_4) δ 1.95 (m, 1 H), 2.35 (m, 3 H), 2.71 (m, 1 H), 2.87 (m, 1 H), 3.17 (m, 1 H), 7.0–7.4 (m, 15 H); mass spectrum *m/e* (rel intensity) 298 (54), 296 (26), 220 (39), 219 (10), 207 (24), 194 (30), 193 (54), 192 (21), 191 (29).

Exact mass (70 eV) calcd for $C_{23}H_{22}$, 298.17226; found 298.17210.

Phenanthrene and 1 HMPA. A solution of 15 mmol of phenanthrene and 15 mmol of 1 HMPA in 50 ml of THF was stirred for 48 h at room temperature. Periodically 5.0-ml aliquots were quenched with aqueous NH_4Cl and extracted with hexane/dichloromethane. GLC–mass spectrometry with column E showed a product with a molecular ion at *m/e* 294 which was isolated by GLC on column B at 290 °C and identified as **10** by its 220-MHz NMR and mass spectra. Its yield maximized at 20% after 18 h. The only other product detected was 9,10-dihydrophenanthrene in a maximum yield of 17% after 80 min: NMR of **10** (CCl_4) δ 3.38 (d of d, J = 13, 6 Hz, 2 H), 3.77 (m, 3 H), 7.0–7.3 (m, 9 H), 7.51 (m, 4 H), 7.73 (m, 2 H), 8.60 (m, 2 H); mass spectrum (70 eV) *m/e* (rel intensity) 296 (5), 295 (32), 294 (100), 292 (15), 280 (10), 279 (44), 278 (14), 259 (12), 219 (13), 218 (13), 217 (14), 216 (41), 215 (28).

To determine the origin of the small *m/e* 296 peak in the mass spectrum, exact mass measurements were made on both the 294 and the 296 peaks: calcd for $C_{23}H_{18}$, 294.1409; found, 294.1407; calcd for $^{13}C_2{}^{12}C_{21}H_{18}$, 296.1477; found, 296.1478.

In an attempt to identify cycloadduct 11 before oxidation to **10**, the reaction was repeated, the entire isolation procedure was carried out in a N_2 atmosphere, and the solution of product in THF and hexane was stored at −20 °C until analysis. GLC–mass spectrometry showed a mass spectrum identical with that obtained when the hydrolyzed reaction mixture was handled in air.

Acenaphthylene and 1 HMPA. A solution of 15 mmol of acenaphthylene and 15 mmol of 1 HMPA in 50 ml of THF was stirred for 4.0 h at room temperature. Periodically 5.0-ml aliquots of the solution were quenched in aqueous NH_4Cl, extracted with hexane/dichloromethane, and analyzed by GLC on column E. GLC–mass spectrometry showed only one product, which had a molecular ion at *m/e* 270. Its yield maximized at 43% after 1.0 min. It was isolated by GLC on column C at 300 °C and was identified by 220-MHz NMR and mass spectra as **12**: NMR (CCl_4) δ 2.65 (d of d, H_a, J_{ab} = 14.5, J_{ac} = 10 Hz), 3.04 (d of d, H_e, J_{de} = 17, J_{ce} = 3 Hz), 3.11 (d of d, H_b, J_{bc} = 5 Hz), 3.40 (d of d, H_d, J_{cd} = 8 Hz), 3.73 (m, H_c), 5.14 (s, H_g), 5.26 (s, H_f), 7.1–7.6 (m, 11 H); mass spectrum *m/e* (rel intensity) 270 (5), 253 (3), 189 (2), 165 (16), 154 (30), 153 (100), 152 (100), 127 (4), 126 (5), 115 (22).

Exact mass calcd for $C_{21}H_{18}$, 270.1409; found, 270.1410.

Anthracene and 1 HMPA. A solution of 15 mmol of anthracene and 15 mmol of 1 HMPA in 50 ml of THF was stirred for 98 h at room temperature. Periodically 5.0-ml aliquots of the solution were quenched in aqueous NH_4Cl, extracted with hexane/dichloromethane, and analyzed by GLC on column E. An aliquot taken after 0.5 min showed a single peak in 51.5% yield. Subsequent aliquots showed two GLC peaks. The first decreased and the second increased in area with time until after 98 h their yields were 6 and 27%, respectively. By GLC–mass spectrometry both compounds had molecular ions at *m/e* 296. 9,10-Dihydroanthracene also was detected by GLC–mass spectrometry. Its yield maximized at 8% after 18 h and then decreased to 0.7% after 98 h.

The reaction was repeated twice. One mixture was hydrolyzed after 0.5 min and the other after 98 h. After the usual extractions and drying, anthracene was precipitated from the first mixture by addition of hexane. Removal of solvent and α-methylstyrene under vacuum left a light yellow oil which was chromatographed with hexane over a 1 × 20 cm column of silica gel. Evaporation of solvent left a colorless oil which was stored at −10 °C under vacuum because it turned yellow when exposed to air. GLC analysis of yellowed material showed several new peaks in addition to the compound originally isolated. The colorless oil was identified as acyclic adduct **13** by its 220-MHz NMR and mass spectra: NMR (CCl_4) δ 2.70 (br d, H_a, J_{ab} = 7 Hz), 3.82 (d, H_d, J_{cd} = 18.5 Hz), 3.88 (t, H_b), 3.96 (br d, H_c), 4.50 (br d, H_f, J_{ef} = 2 Hz), 5.10 (d, H_e), 6.8–7.5 (m, 13 H); mass spectrum (70 eV) *m/e* (rel intensity) 296 (0.69), 294 (3.98), 181 (9), 180 (85), 179 (100), 178 (98), 177 (26), 176 (38), 152 (20), 151 (15).

Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.19; H, 6.94.

The product from the reaction mixture hydrolyzed after 98 h was isolated by GLC on column B at 290 °C and identified as **14** by its 220-MHz NMR and mass spectra: NMR (CCl_4) δ 1.69 (t, H_b, J_{ab} = J_{bc} = 12 Hz), 2.06 (quintet, H_a, J_{ac} = J_{ad} = 6 Hz), 2.21 (m, H_c), 4.02 (d, H_d), 6.75–7.25 (m, 13 H); mass spectrum (70 eV) 296 (83), 219 (9), 218 (45), 217(17),203(14),193(21),192(99),191(96),190(17), 189(35).

Exact mass (70 eV) calcd for $C_{23}H_{20}$, 296.1566; found, 296.1565.

α,α′-Difluorostilbene[33] was prepared by reaction of tetrafluoroethylene and phenyllithium[34] in THF at −78 °C and recrystallized from 95% ethanol: mp 72–73 °C (lit.[33] mp 74 °C); ^{19}F NMR (CCl_4) δ 154.3 ppm from $CFCl_3$ (s, $J_{^{13}CCF}$ = 92, $J_{^{13}CF}$ = 281, J_{FF} = 121 Hz).

α,α′-Difluorostilbene and 1 HMPA. A solution of 15 mmol of difluorostilbene and 15 mmol of 1 HMPA in 50 ml of THF was stirred for 4.0 h at room temperature. Periodically 2.0-ml aliquots of the solution were analyzed by GLC on column E. Two products were detected in 12.7 and 1.4% yield after 1.0 min. Both had molecular ions at *m/e* 314 by GLC–mass spectrometry. They were isolated separately by GLC on column A at 290 °C and identified by their ^{1}H NMR, ^{19}F NMR, and mass spectra as isomers of 1,2,4-triphenyl-1-fluoro-1,4-pentadiene **15a** and **15b:** NMR (CCl_4) of major isomer δ 3.57 (m, 2 H), 5.15 (m, 1 H), 5.30 (m, 1 H), 7.0–7.6 (m, 15 H); ^{19}F NMR δ 99.6 (s); mass spectrum (70 eV) *m/e* (rel intensity) 314 (100), 295 (6), 294 (18), 238 (4), 237 (16), 236 (83), 235 (13), 224 (16), 223 (83), 222 (13).

Exact mass calcd for $C_{23}H_{19}F$, 314.14717; found 314.14643.

NMR (CCl_4) of minor isomer δ 3.72 (m, 2 H), 4.99 (m, 1 H), 5.18 (m, 1 H), 6.7–7.5 (m, 15 H); ^{19}F NMR δ 99.6 (s); mass spectrum (70 eV) *m/e* (rel intensity) 314 (100), 295 (4), 294 (15), 238 (2), 237 (15), 236 (61), 235 (11), 224 (12), 223 (39), 222 (12). The yields of the two isomers were 13 and 2% in samples taken from 1.0 min to 4 h reaction time.

***trans*-1,1,1,4,4,4-Hexafluoro-2,3-diphenyl-2-butene (16)**[35] was prepared by reaction of phenyllithium and perfluoro-2-butene at room temperature and recrystallized from ethanol, mp 181–182 °C (lit.[35] mp 179–181 °C).

16 and 1 HMPA. A solution of 3.0 mmol of 1 HMPA in 10 ml of THF was chilled to 0 °C and added to 3.0 mmol of **16.** The mixture was stirred at 0 °C and sampled as usual. GLC–mass spectrometry with column E showed a single sharp product peak with a molecular ion at *m/e* 414. Its yield maximized at 38% after 90 min. This material was isolated by GLC on column A at 260 °C and identified by its 60-MHz ^{1}H NMR, ^{19}F NMR, and mass spectra as a 70/30 mixture of isomers **17a** and **17b.** NMR (CCl_4) of major isomer δ 2.82 (t, J_{HF} = 17 Hz, 2 H), 4.94 (m, 1 H), 5.31 (m, 1 H), 6.7–7.3 (m); ^{19}F NMR δ 84.3 (t, *J* = 2 Hz, 3 H), 85.6 (t, *J* = 17 Hz, 2 H).

NMR of minor isomer δ 3.20 (t, J_{HF} = 17 Hz, 2 H), 5.25 (m, 1 H), 5.43 (m, 1 H), 6.7–7.3 (m). ^{19}F NMR same as major isomer; mass spectrum of mixture (70 eV) *m/e* (rel intensity) 414 (13), 413 (47), 394 (12), 290 (11), 278 (13), 277 (60), 180 (100). The composition of the mixture did not change in samples taken from 1.5 to 91 h.

Anal. of mixture. Calcd for $C_{25}H_{19}F_5$: C, 72.46; H, 4.62. Found: C, 72.36; H, 4.62.

2-[(*E*)-2-Phenylethenyl]-4,4-dimethyloxazoline (18). By a general procedure[36] 0.44 mol of 2-amino-2-methyl-1-propanol and 0.22 mol of cinnamoyl chloride gave a 67% yield of *N*-(2,3-dimethyl-3-hydroxypropyl)cinnamide (**22**), mp 133–134 °C.

Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.81; N, 6.38. Found: C, 71.38; H, 7.91; N, 6.40.

Treatment of 0.15 mol of **22** with 0.31 mol of thionyl chloride by a general procedure[36] gave a colorless oil which was distilled to give a 32% yield of **18**, bp 187 °C (25 mm) [lit.[37] bp 112–120 °C (0.4–0.6 mm)].

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.57; H, 7.51; N, 6.90. Found: C, 77.72; H, 7.28; N, 7.22.

18 and 1 HMPA. A solution of 15.0 mmol of **18** and 15.0 mmol of 1 HMPA in 50 ml of THF was stirred for 22 h at room temperature. Periodically 5.0-ml aliquots were quenched in 50% aqueous $NaHCO_3$, washed with two portions each of dilute NaOH, dilute $NaHCO_3$, and water, and dried over $MgSO_4$. GLC on column E showed a single product which had a molecular ion at *m/e* 319 by GLC–mass spectrometry. It was isolated by liquid chromatography on a 3 × 60 cm silica gel column at a flow rate of 1000 ml/h of 78% dichloromethane, 20% acetonitrile, and 2% diethyl ether (by volume) in the fractions collected between 800 and 1700 ml of eluate. After evaporation of solvent, the remaining colorless oil was identified as **19** by its IR, ^{1}H NMR, and mass spectra, and by chemical conversion to **21b.** NMR (CCl_4) of **19** δ 1.00 (s, 3 H), 1.09 (s, 3 H), 2.48 (AB q of d, Δδ = 27 Hz, H_a at δ 2.42 and H_b at δ 2.54, J_{ab} = 15, J_{ac} = 8, J_{bc} = 7 Hz), 2.70 (d of d, H_d, J_{cd} = 8.5, J_{de} = 14 Hz), 3.01 (d of d, H_e, J_{ce} = 6 Hz), 3.14 (m, H_c), 3.59 (s, 2 H), 4.81 (m, 1 H), 5.13 (m, 1 H), 7.0–7.3 (m, 10 H); IR (neat) 3060 (m), 2990 (s), 1670 (s), 1450 (m), 1360 (m), 1270 (s), 1200 (s), 1040 (m), 1000 (s), 900 (m), 775 (s), 710 cm^{-1} (s); mass spectrum (70 eV) *m/e* (rel intensity) 319 (5), 201 (32), 200 (19), 187 (15), 186 (100), 170 (12), 158 (11), 130 (29), 115 (29), 113 (14).

Exact mass calcd for $C_{22}H_{25}NO$, 319.1938; found, 319.1933.

3,5-Diphenyl-4-hexenoic Acid (21a). Oxazoline **19** (4.3 g) was hydrolyzed in 15 min in boiling 3 N HCl to 3.6 g of waxy solid, which was purified by liquid chromatography through a 3 × 60 cm column of silica gel with 10% methanol in CH_2Cl_2 (by volume). The recovered white solid was identified as **21a** by IR, NMR, and mass spectra and reduction to alcohol **21b:** NMR (CCl_4) δ 2.1 (d, *J* = 1 Hz, CH_3), 2.75 (d, *J* = 8 Hz, $H_a + H_b$), 4.2 (q, H_c), 5.85 (d, J_{cd} = 9 Hz, H_d), 7.3 (br s); IR (KBr) 3090 (m), 2950 (m), 1710 (s), 1500 (m), 1450 (m), 1420 (m), 1300 (m), 1260 (m), 950 (m), 760 (s), 700 cm^{-1} (s); mass spectrum (70 eV) *m/e* (rel intensity) 266 (20), 251 (12), 208 (18), 207 (98), 206 (15), 192 (11), 191 (26), 178 (13), 130 (14), 129 (100), 127 (26).

Exact mass calcd for $C_{18}H_{18}O_2$, 266.13047; found, 266.13042.

3,5-Diphenyl-4-hexen-1-ol (21b). By a general procedure[38] 1.4 g of **21a** was reduced with $LiAlH_4$ in THF to a light yellow oil. Chromatography through a 3 × 60 cm silica gel column with 2% diethyl ether in CH_2Cl_2 gave 1.05 g of a colorless oil. GLC analysis on column E showed three sharp peaks with relative areas of 6.25, 8.75, and 85.0, respectively. GLC–mass spectrometry showed molecular ions at *m/e* 252 and nearly identical fragmentation patterns for all three compounds. The major component of the oil was identified by Eu(fod)$_3$-shifted NMR spectra of the mixture as **21b** (see Results): NMR (CCl_4) δ 2.1 (d, *J* = 2 Hz, CH_3), 1.9 (q, *J* = 7 Hz, $H_a + H_b$), 2.5 (br s, OH), 3.55 (t, *J* = 7 Hz, CH_2OH), 3.85 (m, $J_{ac} = J_{bc}$ = 7, J_{cd} = 9 Hz, H_c), 5.9 (br d, H_d), 7.2 (m); IR of mixture (C_2Cl_4) 3620 (m), 3080 (m), 3060 (m), 3040 (s), 2940 (s), 1600 (m), 1500 (s), 1450 (m), 1400 (m), 1380 (m), 1050 cm^{-1} (s); mass spectrum (70 eV) *m/e* (rel intensity) 252 (16), 219 (13), 208 (23), 207 (100), 178 (10), 129 (13), 128 (78), 127 (16), 118 (27), 116 (27).

Exact mass calcd for $C_{18}H_{20}O$, 251.1515; found, 251.1515.

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.98. Found: C, 85.41; H, 7.98.

α-Methylstyrene, *trans*-Stilbene, and LDIA. To a solution of 15.0 mmol of LDIA in 50 ml of THF was added 15.0 mmol of α-methylstyrene and 15.0 mmol of *trans*-stilbene, and the solution was held at 45 ± 2 °C for 166 h. Samples of the reaction mixture were isolated and analyzed as described for experiments with 1 HMPA. GLC–mass spectral analyses showed four principal fractions of which the first three were isolated. The first was identified by its 220-MHz ^{1}H NMR spectrum as **2.** Yields of all four components increased throughout the reaction to 27.9, 6.2, 5.7, and 1.3% after 166 h, in order of increasing GLC retention time.

***cis*-Stilbene and LDIA.** A solution of 15 mmol of LDIA and 15 mmol of *cis*-stilbene in 50 ml of THF was held at 45 ± 2 °C. The *cis*-stilbene was 43% isomerized after 0.66 h and 99% isomerized after 19 h by GLC on column D.

***cis*-Stilbene-α,α′-d_2 and LDIA.** A solution of 3.0 mmol of LDIA and 3.0 mmol of *cis*-stilbene-α,α′-d_2 in 10.0 ml of THF was held at 45 °C for 4.5 h and hydrolyzed in the usual manner. Analytical GLC on column D showed 53% *cis*- and 47% *trans*-stilbene. Each isomer was collected by preparative GLC on column A at 230 °C. Deuterium analysis by mass spectrometry showed 90% d_2, 9% d_1, and 1% d_0 for *cis*-stilbene and 50% d_2, 48% d_1, and 2% d_0 for *trans*-stilbene.

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Registry No.—**1**, 58688-36-1; 1 HMPA, 61062-62-2; **2**, 58688-37-2; **3**, 36963-72-1; **4**, 5155-87-3; **5**, 61025-10-3; **7a**, 61025-11-4; **7b**, 61091-26-7; **8a**, 61025-12-5; **8b**, 61025-13-6; **9**, 61025-14-7; **10**, 61025-15-8; **12**, 61025-16-9; **13**, 61025-17-0; **14**, 61025-18-1; **15a**, 61025-19-2; **15b**, 61025-20-5; **16**, 29030-86-2; **17a**, 61025-21-6; **17b**, 61025-22-7; **18**, 61025-23-8; **19**, 61025-24-9; **21a**, 61025-25-0; **21b**, 61025-26-1; α-methylstyrene, 98-83-9; *N*-bromosuccinimide, 128-08-5; 3-bromo-2-phenylpropene, 3360-54-1; 1-bromo-2-phenylpropene, 3360-53-0; chlorotriphenyltin, 639-58-7; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8; *trans*-β-methylstyrene, 873-66-5; *cis*-β-methylstyrene, 766-90-5; 1,1-diphenylethylene, 612-00-0; phenanthrene, 85-01-8; acnaphthylene, 208-96-8; anthracene, 120-12-7; α,α′-difluorostilbene, 20488-54-4; 2-amino-2-methyl-1-propanol, 124-68-5; cinnamoyl chloride, 102-92-1; *N*-(2,3-dimethyl-3-hydroxypropyl)cinnamide, 30687-08-2; LDIA, 4111-54-0; tetrafluoroethylene, 116-14-3; phenyllithium, 591-51-5.

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Rate Enhancement of the Meerwein–Ponndorf–Verley–Oppenhauer Reaction in the Presence of Proton Acids[1]

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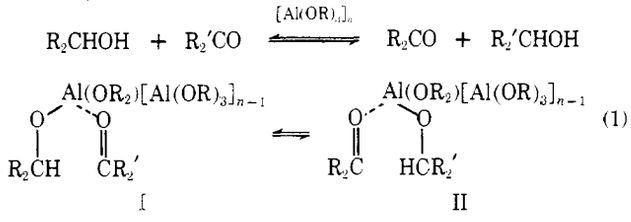
The effects of various protic acids upon the aluminum *tert*-butoxide catalyzed oxidation of cyclohexanol by benzaldehyde are studied. The rate of oxidation is found to be markedly enhanced by an acid to aluminum ratio of 0.5 for HCl, FSO_3H, $CH_3CH_2CO_2H$, and CF_3CO_2H, with CF_3CO_2H giving the greatest rate enhancement. Synthetic applications of this method, however, are limited by the observation that trifluoroacetic acid–aluminum alkoxide mixtures are potent aldol catalysts.

The Meerwein–Ponndorf–Verley–Oppenhauer (MPVO) reaction is the aluminum alkoxide catalyzed equilibration of alcohols with aldehydes or ketones[2], eq 1. A key step in the

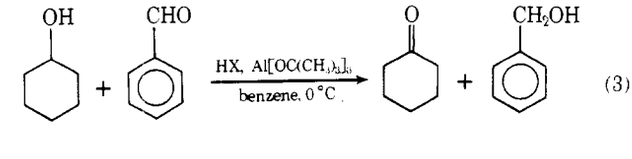


reaction is thought to be hydride transfer within the polymeric aluminum complexes I and II.[3]

Replacement of alkoxy groups on aluminum with more electronegative ligands should increase the rate of MPVO reactions by facilitating coordination of aluminum to the carbonyl compound.[4] This replacement should be achieved most simply by addition of a suitable proton acid (HX) to a solution of the aluminum alkoxide (eq 2).

$$[Al(OR)_3]_n + HX \rightarrow HOR + [XAl(OR)_2]_n \quad (2)$$

For study, we chose the reaction between cyclohexanol and benzaldehyde catalyzed by aluminum *tert*-butoxide in benzene solution at 0 °C (eq 3). The rate of reaction was followed by removing aliquots at various times and analyzing by GLC for cyclohexanone. With a twofold excess of benzaldehyde, equilibrium is established when 88% of the starting cyclohexanol is converted to cyclohexanone. Results obtained in the presence of a variety of proton acids are shown in Table I.



The most effective catalyst is trifluoroacetic acid, present at an acid to aluminum ratio of 0.5. Data obtained with this acid are presented graphically in Figure 1.

With all acids studied, the reaction fails when a critical ratio of acid to aluminum is exceeded. In some cases this is perhaps due to the precipitation of aluminum compounds which occurs with the higher ratios of acid. However, with trifluoroacetic acid no precipitate is formed at an acid to aluminum ratio of 2.0, yet at this point the MPVO reaction fails. It is conceivable that only nonbridging alkoxy groups in complexes I and II are able to transfer hydride[5] and that at a critical acid to aluminum ratio all such groups are replaced with trifluoroacetate ligands.

^1H NMR examination of the catalyst system is hampered by precipitation of aluminum compounds in the absence of added alcohol or aldehyde. Thus, when 0.3 equiv of trifluoroacetic acid was added to aluminum *tert*-butoxide in benzene, a precipitate was formed and ^1H NMR analysis of the supernatent revealed only the normal spectrum of the aluminum *tert*-butoxide dimer[6] together with 0.3 equiv of *tert*-butyl alcohol.