Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.97; H, 5.48; N, 9.59. Found: C, 73.67; H, 5.37; N, 9.55.

Reactions of the Thiirene Dioxides 1a,b with the Dienamine 9. To a solution of **1a** (1.0 g, 4.1 mmol) in benzene (30 mL) was added **9** (0.70 g, 4.1 mmol) at room temperature, and the mixture was stirred at reflux for 5 h. The reaction mixture was concentrated to give 0.85 g (61%) of 1,2-diphenyl-3,5-dimethyl-6-piperidino-1,3-cyclohexadiene (**11**) as a colorless solid upon addition of MeOH: mp 83–84 °C (colorless needles from EtOH); IR 1600 cm^{-1} (C=C); NMR δ 1.07 (d, 3 H, J = 7.6 Hz, Me), 1.3–1.8 (br m, 6 H, 3 CH_2), 1.84 (dd, 3 H, J = 1.6 and 1.6 Hz, Me), 2.1–3.3 (br m, 5 H, 2NCH_2 and CH), 3.75 (d, 1 H, J = 4.8 Hz, NCH), 5.68 (dq, 1 H, J = 4.4 and 1.6 Hz, =CH), 6.7–7.4 (m, 10 H, 2 Ph); MS, m/e 343 (M^+).

Anal. Calcd for $C_{25}H_{29}N$: C, 87.46; H, 8.45; N, 4.08. Found: C, 87.16; H, 8.40; N, 4.05.

Compounds **1b** (1.0 g, 8.5 mmol) and **9** (1.4 g, 8.2 mmol) were allowed to react in refluxing benzene for 11 h to give 12% (determined by GLC) of 1,2,3,5-tetramethylbenzene, whose IR and NMR spectra were in good agreement with those of an authentic sample.

Acidic Treatment of the Dihydrobenzene 11. A solution of **11** (0.4 g, 1.2 mmol) and 2 N HCl (6 mL) in EtOH (10 mL) was refluxed for 3 h. The reaction mixture was neutralized and extracted (Et_2O). The organic extract was dried (Na_2SO_4) and distilled to give 0.26 g (100%) of 3,5-dimethyl-1,2-diphenylbenzene (**12**): bp 93–97 °C (2 mmHg) by pot distillation; NMR (CCl_4) δ 2.10 (s, 3 H, Me), 2.37 (s, 3 H, Me), 6.9–7.3 (m, 12 H, aromatic protons); MS, m/e 258 (M^+).

Anal. Calcd for $C_{20}H_{18}$: C, 93.02; H, 6.98. Found: C, 92.84; H, 7.21.

Registry No. **1a**, 5162-99-2; **1b**, 30646-57-2; **2**, 15409-32-2; **4a**, 7189-13-1; **4b**, 7189-14-2; **5**, 73935-66-7; **7a**, 73935-71-4; **8a**, 73935-70-3; **8b**, 73935-69-0; **9**, 10321-86-5; 11, 88946-44-5; **12**, 73935-73-6; N-phenylbenzhydrazidoyl chloride, 15224-14-3; N-benzyl-p-nitrobenzimidoyl chloride, 3712-57-0; 1,2,3,5-tetramethylbenzene, 527-53-7.

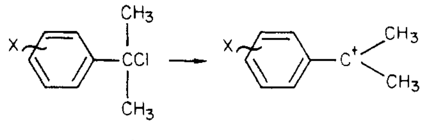
Gas-Phase Basicities of Substituted Styrenes. Comparison of Gas-Phase and Solution Reactivities

Alex G. Harrison,*[1a,b] Raymond Houriet,[1a] and
Thomas T. Tidwell*[1b]

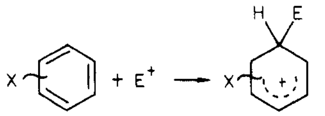
Institut de Chimie Physique, École Polytechnique Fédérale, Lausanne, Switzerland, and the Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1

Received May 13, 1983

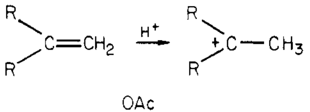
One of the most successful quantitative treatments for the understanding of organic reactions in solution has been the use of the Brown–Hammett σ^+ constants for the correlation of electrophilic reactivity.[2] These parameters are defined[3] in terms of the solvolysis of cumyl chlorides at 25 °C (eq 1) by the equation $\log k(X)/k(H) = -4.54\sigma^+$.



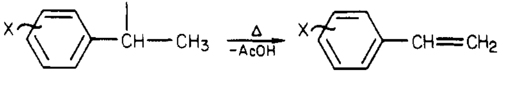
(1)



(2)



(3)

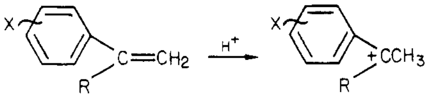


(4)

The σ^+ constants derived from eq 1 account quite successfully for a variety of electrophilic aromatic substitution reactions, as illustrated in eq 2. These constants also have been found to correlate reactivities in a variety of other systems, including the rates of protonation of aliphatic alkenes (eq 3),[4] and the gas-phase pyrolysis of 1-arylethyl acetates to form styrenes (eq 4).[5]

With the increasing availability of values of gas-phase heats of reaction[6] as well as the heats of formation of carbocations in solution,[7] it has become increasingly possible to evaluate the contributions of ion stability and solvation to organic reactivity and to compare the rates of reaction in solution with heats of reaction. A notable achievement in this field was the measurement of the gas-phase basicities of substituted benzenes.[8a] These were found to be correlated very well with the σ^+ constants, which was a powerful indication that these empirically derived quantities did, in fact, provide a quantative measure of substituent effects on cation stability. The thermodynamics of these reactions also can be accounted for by molecular orbital calculations.[8b,9]

The correlations of the rates of protonation of styrenes in solution (eq 5) is another case where the σ^+ constants have been very successful.[10] The relations between the sensitivity of the reaction to the substituents X, which is measured by the ρ^+ values, and the electron-donating ability of the substituent R, as measured by the σ^+ value of this group, also has been revealing. It has been found[10h] that when R is strongly electron-donating (HO,[10d] MeO[10e], EtO[10f]), ρ^+ has values between −1 and −2, whereas when R is strongly electron-withdrawing (CF_3), ρ^+ is −4.0.[10h] Intermediate situations exist when R = H (ρ^+ = −2.9,[10b] −3.6[10c,i]), and R = Me (ρ^+ = −2.9[10a,b]).



(5)

1, R = H
2, R = CH_3

---

[1] (a) Institut de Chimie Physique, École Polytechnique Fédérale, Lausanne, Switzerland. (b) Department of Chemistry, University of Toronto, Toronto Canada M5S 1A1.

[2] Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *2* 35–154.

[3] Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979–4987.

[4] Nowlan, V. J.; Tidwell, T. T. *Acc. Chem. Res.* **1977**, *10*, 252–258.

[5] (a) Hossaini, M. A.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1982**, 187–190. (b) Glyde, E.; Taylor, R. Ibid. **1977**, 1537–1541 and other papers in this series.

[6] Hartman, K. N.; Lias, S.; Ausloos, P.; Rosenstock, H. M.; Schroyer, S. S.; Schmidt, C.; Martinsen, D.; Milne, A. "A Compendium of Gas-Phase Basicity and Proton Affinity Measurements"; U.S. Department of Commerce, Washington, DC, 1979; NBSIR 79-1977.

[7] Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2889–2895 and previous papers in this series.

[8] (a) Lau, Y. K.: Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 7452–7453. (b) McKelvey, J. M.; Alexandratos, S.; Streitwieser, A., Jr.; Abboud, J.-L.; Hehre, W. J. *Ibid.* **1976**, *98*, 244–246.

[9] Vorpagel, E. R.; Streitwieser, A., Jr.; Alexandratos, S. P. *J. Am. Chem. Soc.* **1981**, *103*, 3777–3781.

[10] (a) Deno, N. C.; Kish, F. A.; Peterson, H. J. *J. Am. Chem. Soc.* **1965**, *87*, 2157–2161. (b) Simandoux, J. C.; Torck, B.; Hellin, M.; Coussemant, F. *Bull. Soc. Chim. Fr.* **1972**, 4402–4409. (c) Keeffe, J. R.; Schubert, W. M. *J. Am. Chem. Soc.* **1972**, *94*, 559–566. (d) Dubois, J.-E.; El-Alaoui, M.; Toullec, J. *Ibid.* **1981**, *103*, 5393–5401. (e) Loudon, G. M.; Berke, C. *Ibid.* **1974**, *96*, 4508–4517. (f) Chiang, Y.; Chwang, W. K.; Kresge, A. J.; Robinson, L. H.; Sagatys, D. S.; Young, C. I. *Can. J. Chem.* **1978**, *56*, 456–460. (g) Allen, A. D.: Rosenbaum, M.; Seto, N. O. L.; Tidwell, T. T. *J. Org. Chem.* **1982**, *47*, 4234–4239. (h) Koshy, K. M.; Roy, D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1979**, *101*, 357–363. (i) Ellis, G. W. L.; Johnson, G. D. *J. Chem. Soc. Perkin Trans. 2* **1982**, 1025–1027.

0022-3263/84/1949-1302$01.50/0

Table I. Gas-Phase Basicities (GB) of Styrenes $XC_6H_4CR{=}CH_2$

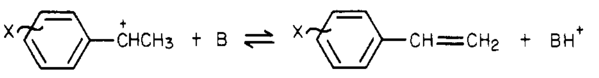
X	GB, kcal/mol^{-1}		σ^+
	R = H (1)	R = Me (2)[a]	
p-MeO	207.4	209.5	−0.78
p-Me	199.8	203.5	−0.31
p-F		199.6	−0.07
H	195.2[b]	199.7[b]	0.0
p-Cl		197.9	0.11
p-Br	194.3		0.15
m-Br	190.4		0.40
m-CF_3	187.6		0.52
p-CF_3		192.0	0.61

[a] These data are reported in ref 6 with reference to $GB(NH_3)$ = 193.7 kcal mol^{-1}. They are reported here relative to $GB(NH_3)$ = 196.4 kcal mol^{-1} the scale used for the styrenes. [b] Gas-phase basicities of 194.4 kcal mol^{-1} for styrene and 199.8 kcal mol^{-1} for α-methylstyrene have been reported earlier.[13]

A correlation of calculated proton affinities for α-methylstyrenes (eq 5, R = Me) with known gas-phase proton affinities for these substrates has recently appeared.[11] Because of the central position that this system occupies in the correlation of organic reactivity it is highly desirable to extend this study to other R groups as shown in eq 5.

Experimental Section

The gas-phase basicities, GB, of styrene, *p*-methoxystyrene, *p*-methylstyrene, *p*-bromostyrene, *m*-bromostyrene, and *m*-trifluoromethylstyrene were determined by measuring equilibrium constants for the proton-transfer reaction 6 using reference bases



(6)

of known basicity. The experiments were performed with an ICR spectrometer built at the EPF-Lausanne and operated under conditions similar to those described previously.[12] From two to five measurements were carried out for each sample by using at least two different reference bases. All measurements were made at 323 K and are referenced to $GB(NH_3)$ = 196.4 kcal mol^{-1};[13] the uncertainty in the reported gas-phase basicities is ±0.2 kcal mol^{-1}. All compounds used were commercial samples of high purity and showed no detectable impurities in their mass spectra.

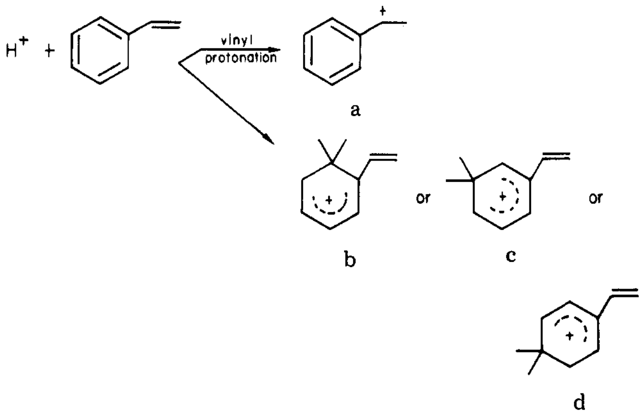
Results and Discussion

The gas-phase basicities measured for the group of styrenes 1 with different aryl substituents are tabulated in Table I. Also included in the table are literature values of the gas-phase basicities of aryl-substituted α-methylstyrenes 2[6] and values of σ^+ for the substituents.[3] The gas-phase basicities are correlated with σ^+ values by the equations GB = $-14.6\,\sigma^+ + 195.7$ ($r = 0.997$) for 1 and GB = $12.6\,\sigma^+ + 199.4$ ($r = 0.997$) for 2. The gas-phase basicities represent $-\Delta G°$ for reaction 7 and are the most

$$H^+ + XC_6H_4C(R){=}CH_2 \rightleftharpoons XC_6H_4C^+(R)CH_3 \quad (7)$$

appropriate quantities to correlate with σ^+ since Hammett-type relationships are linear free energy relationships. One would anticipate that for each reaction series the entropy change ($\Delta S°$) for reaction 7 should be constant with the result that gas-phase proton affinities ($-\Delta H_7°$) will correlate with σ^+ with the same slopes. For example, Lau and Kebarle[8a] have shown that $\Delta S°$ for protonation of chlorobenzene and fluorobenzene was in agreement with the entropy change expected solely from the change in rotational symmetry number and they analyzed the data on the protonation of other substituted benzenes on this basis.

Scheme I



Protonation of styrene can occur either on the vinyl or on the phenyl group according to the reaction in Scheme I. Gas-phase basicities for styrene and α-methylstyrene (195.2 and 199.7 kcal mol^{-1}, respectively) compared to GB(toluene) = 185.2 kcal mol^{-1} [13] indicate that protonation of styrene under equilbrium conditions probably occurrs on the vinyl group to form the methylbenzylcation a. This is in agreement with McLafferty and co-workers[14] who concluded from collisional activation studies that protonation of styrene yielded the methylbenzyl cation. It also is in accordance with ab initio (STO 3-G) calculations[15] on $C_8H_9^+$ that predict the methylbenzyl ion to be more stable than ring-protonated styrene by at least 20 kcal mol^{-1}.

We attempted to obtain an experimental confirmation of this basicity difference by carrying out experiments with styrene-*2,3,4,5,6*-d_5 (Merck, Sharp & Dohme, 99.5 D atom %). Under equibibrium conditions we observed *no* back-transfer of D^+ to the partner B (reaction 6), in accordance with the fact that vinyl protonation occurs under these conditions. We tried further to ring-protonate the styrene-d_5 by using the strong Brøonsted acids CH_5^+ and $C_2H_5^+$, formed in methane, in the presence of a strong base B. This procedure should allow the detection of BD^+ product ions providing that B is more basic than styrene (for details concerning the experimental procedure for the determination of relative basicities in multifunctional bases, see ref 12). Under these conditions we could not detect any BD^+ products with reference bases B ranging up to ammonia (GB = 196.4 kcal mol^{-1}) in basicity. These results suggest that interaction of the proton with the phenyl group in styrene does not lead to a product existing in a potential minimum (or, in other words, not sufficiently long-lived to render the incoming proton equivalent with the ring deuterium atoms) but that the H^+–styrene complex collapses to the vinyl-protonated structure. It might also be that a structure such as the phenonium ion is attained; such a structure has been calculated[15] to be less stable than the methylbenzyl ion by only 6 kcal mol^{-1}. Detailed calculations on the potential energy surface between these structures should provide a confirmation of our observations.

The excellent correlations provide further powerful confirmation of the utility of the σ^+ constants as a measure

---

(11) Greenberg, A.; Liebman, J. F. *J. Org. Chem.* **1982**, *47*, 2084–2088.

(12) Houriet, R.; Schwarz, H.; Zummack, W.; Andrade, J. G.; Schleyer, P. v. R. *Nouv. J. Chim.* **1981**, *5*, 505–509.

(13) Aue, D. H.; Bowers, M. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 9.

(14) Koppel, C.; Van de Sande, C. C.; Nibbering, N. M. M.; Nishishita, T.; McLafferty, F. W. *J. Am. Chem. Soc.* **1977**, *99* 2882–2888.

(15) Hehre, W. J. In "Modern Theoretical Chemistry"; Schaeffer, H. F., Ed.; Plenum Press: New York, 1977; Vol. 4; p 324.

of ion stability in solution. The distinctly greater sensitivity of the correlation of the styrenes **1** ($\rho^+ = -10.9$[16]) than for the methylstyrenes **2** ($\rho^+ = -9.4$) also fits the general expectations for solution-phase reactions. In solution the most recent values for the reaction of **1** in H_2SO_4 ($\rho^+ = -3.6$)[10i] and in $HClO_4$ ($\rho^+ = -3.6$)[10c] and the value for **2** in H_2SO_4 ($\rho^+ = -2.9$)[10a,b] follow a similar trend but with a significantly reduced magnitude. An earlier value for **1** in H_2SO_4 ($\rho^+ = -2.9$)[10b] is somewhat different, however there are several of the data points for the H_2SO_4 rates that show noteable deviations from these correlations, so that the overall reliability of the ρ^+ value is not great. We have suggested elsewhere[10g] that one cause of these deviations might be hydrogen-bonding interactions of the acidic solvents with some of substituents diminishing the electron-donating ability of the substituents. This complication does not occur in the gas phase, and similar deviations from the correlation are not observed. The successful correlation of the protonation of the styrenes by σ^+ in both the solution and the gas phase indicates that the difference in solvation energies of the reactants and transition state ($\Delta G^\circ_{solv} - \Delta G^\ddagger_{solv}$) are either constant or proportional to the substituent stabilization of the cations.

The fact that system **1** has a greater sensitivity to substituent effects than does **2** is in accord with the trends in the gas-phase basicities of methylamines, which show a diminishing ability of methyl groups to stabilize the cation as the cation becomes more stable. Thus, the reported basicities of NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ reveal successive methyl-stabilizing increments of 9.3, 6.6, and 4.2 kcal mol^{-1}. While the stabilizing effect of the methyl group in the styrenes is similar in magnitude to that observed in the methylamines, it is considerably less than that observed in aliphatic alkenes. Thus, recent values reported[17] for the proton affinities of $CH_2{=}CH_2$, $CH_3CH{=}CH_2$, and $(CH_3)_2C{=}CH_2$ are 162.3, 178.7, and 195.5 kcal mol^{-1}, respecively, corresponding to methyl stabilization increments of 16.4 and 16.8 kcal mol^{-1}, respectively. (It should be noted, however, that earlier proton affinities [13] of 163.5, 184.9, and 196.9 kcal mol^{-1} lead to mehyl stabilization increments of 21.4 and 12.0 kcal mol^{-1}, respectively.) No matter which set of data are used, comparison of these data with GB($PhCMe{=}CH_2$) − GB($PhCH{=}CH_2$) = 4.5 kcal mol^{-1} clearly shows a diminished methyl stabilizing effect in the aromatic system due to extensive delocalization of the charge in the aromatic ring in the protonated species.

Acknowledgment. We are indebted to the Natural Sciences and Engineering Research Council of Canada and the Fonds National Suisse de la Rêcherche Scientifique for financial support. A.G.H. gratefully acknowledges a sabbatical leave from the University of Toronto during which this work was carried out.

Registry No. p-$MeOC_6H_4CH{=}CH_2$, 637-69-4; p-$MeC_6H_4CH{=}CH_2$, 622-97-9; p-$FC_6H_4CH{=}CH_2$, 405-99-2; $HC_6H_4CH{=}CH_2$, 100-42-5; p-$ClC_6H_4CH{=}CH_2$, 1073-67-2; p-$BrC_6H_4CH{=}CH_2$, 2039-82-9; m-$BrC_6H_4CH{=}CH_2$, 2039-86-3; m-$CF_3C_6H_4CH{=}CH_2$, 402-24-4; p-$CF_3C_6H_4CH{=}CH_2$, 402-50-6; p-$MeOC_6H_4CMe{=}CH_2$, 1712-69-2; p-$MeC_6H_4CMe{=}CH_2$, 1195-32-0; p-$FC_6H_4CMe{=}CH_2$, 350-40-3; $HC_6H_4CMe{=}CH_2$, 98-83-9; p-$ClC_6H_4CMe{=}CH_2$, 1712-70-5; p-$BrC_6H_4CMe{=}CH_2$, 6888-79-5; m-$BrC_6H_4CMe{=}CH_2$, 25108-58-1; m-$CF_3C_6H_4CMe{=}CH_2$, 368-79-6; p-$CF_3C_6H_4CMe{=}CH_2$, 55186-75-9.

---

(16) The slope, m, of the GB − σ^+ correlation gives ρ^+ from the relation $\rho^+ = 1000\ m/2.303RT$.

(17) Traeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3647-3652.

2-Chloro-4(*R*),5(*R*)-dimethyl-2-oxo-1,3,2-dioxaphospholane, a New Chiral Derivatizing Agent

Robert C. Anderson* and Michael J. Shapiro*

Preclinical Research, Sandoz, Inc., East Hanover, New Jersey 07936

Received November 1, 1983

The utility of chiral derivatizing agents (CDAs) in the study of enantiomeric purity by NMR is well documented.[1] Two of the major problems associated with using CDAs are the observation and resolution of appropriate signals in complex NMR spectra and the potential for asymmetric induction during the preparation of the derivatized substrate. While Mosher's reagent[1] and others[2] eliminate the first concern by utilizing ^{19}F NMR, asymmetric induction can still be a problem.[3] Additionally, ^{19}F NMR is not routinely available to most synthetic chemists.

With these problems in mind, the new CDA **1** has been developed, which has a distinct advantage over those presently available. It is easy to use, and analysis of enantiomeric purity is performed by ^{31}P NMR,[4] a nucleus readily available in NMR systems having broad-band capabilities. The reagent is unique in that either retention or inversion at phosphorus during derivatization[5] of an enantiomerically pure alcohol yields a single diastereomer due to the C_2 symmetry of the chiral glycol ligand on phosphorus.

The synthesis of racemic dioxaphospholane **1** has been reported[6] and was followed here by using (*R*,*R*)-(−)-2,3-butanediol,[7] as shown in Scheme I, to produce the enantiomerically pure CDA **1**.[8]

We have used this new CDA on a variety of alcohols and the results are shown in Table I. The ^{31}P chemical shift range of all of the derivatized alcohols studies is between 12 and 15 ppm while CDA **1** can be found at 17.4 ppm. With slower reacting alcohols such as **12**, an uncharacterized byproduct from reaction of CDA **1**, triethylamine, and DMAP was observed at 1.2 ppm.[9] Except for menthol (**10**), all studies were performed with racemic mixtures to test the extent of asymmetric induction during derivatization and to determine the degree of ^{31}P NMR nonequivalence. The results appear quite good over a range of alcohols, especially in light of the ease of the experimental technique. In spite of the fact that CDA **1** produces diastereomers wherein the interacting asymmetric centers are further apart than those in the diastereomers created by using Mosher's reagent, the ^{31}P NMR nonequivalences using CDA **1** are comparable to those obtained with ^{19}F

---

(1) (a) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 3543-2147. (b) Sullivan, G. r.; Dale, J. A.; Mosher, H. S. *Ibid.* **1973**, *38*, 2143-2147. (c) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512-519.

(2) Pirkle, W. H.; Simmons, K. A. *J. Org. Chem.* **1981**, *46*, 3239-3246.

(3) Dutcher, J. S.; MacMillan, J. G.; Heathcock, C. H. *J. Org. Chem.* **1976**, *41*, 2663-2669.

(4) Mikolayczyk, M.; Omelanczuk, J.; Leitloff, M.; Drabowicz, J.; Ejchart, A.; Jurczak, J. *J. Am. Chem. Soc.* **1978**, *100*, 7003-7008.

(5) Wadsworth, W. S.; Larsen, S.; Horten, H. L. *J. Org. Chem.* **1973**, *38*, 256-263.

(6) Shagidullin, R. R; Shakirov, I. Kh.; Plyamovatyi, A. Kh.; Gurarii, L. I.; Mukmenev, E. T. *Zh. Obsch. Khim.* **1976**, *46*, 1021-1026.

(7) Aldrich Chemical Co.

(8) Reagent **1** and, to a lesser extent, the phosphorylated alcohols are susceptible to moisture. Appropriate precautions are, therefore, warranted. To the NMR tube of derivatized alcohol **11** was added a few drops of water. The tube was shaken vigorously for several minutes and then the ^{31}P NMR was monitored for 15 min. No change in the ratio of the diastereomers was observed.

(9) CDA **1** (1.0 equiv), triethylamine (1.5 equiv), and DMAP (0.1 equiv) were combined and spectra taken. The peak for CDA **1** at 17.4 ppm disappeared completely within 15 min and a new peak at 1.2 ppm appeared.