dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave a liquid which was distilled at 63° (2.7 mm). The sample was induced to crystallize and was recrystallized from petroleum ether (bp 61–70°) giving mp 39–40° (lit.[16] mp 40°).

Registry No.—Phenacyl chloride, 532-27-4; phenacyl bromide, 70-11-1; p-NO$_2$-phenacyl bromide, 99-81-0; p-Cl-phenacyl bromide, 536-38-9; p-Br-phenacyl bromide, 99-73-0; m-CH$_3$O-phenacyl bromide, 5000-65-7; p-CH$_3$O-phenacyl bromide, 2632-13-5; t-butyl phenacyl ether, 7616-91-3; phenacyl formate, 614-20-0.

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The Silver Ion Assisted Solvolysis of Phenacyl Halides in Aqueous Ethanol[1]

D. J. PASTO AND K. GARVES

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

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The kinetics of the silver ion assisted solvolyses of phenacyl chloride, bromide, and iodide, in 50, 80, and 95% aqueous ethanol have been measured at three temperatures. The Hammett ρ value determined for substituted phenacyl bromides in 80% aqueous ethanol at 70° was found to be approximately 0 compared to +0.35 for the unassisted solvolysis. The rate data for the silver ion assisted solvolyses are compared with the rate data reported for the silver ion assisted solvolyses of other alkyl halides and the rate data for the unassisted solvolyses. The mechanism of the silver ion assisted solvolysis of phenacyl bromide is best described as a highly concerted push–pull mechanism (electrophically assisted nucleophilic displacement). The carbon atom undergoing substitution possesses slightly greater carbonium ion character in the silver ion assisted solvolysis than in the unassisted solvolysis. The role of silver ion as the electrophilic catalyst in the transition state is discussed. A linear correlation is observed between the enthalpies of activation for the silver ion assisted solvolysis of phenacyl chloride, bromide, and iodide and the difference in silver–halogen and carbon–halogen bond energies. It is concluded that extensive silver–halogen and carbon–oxygen bond formation and carbon–halogen bond cleavage have occurred in going to the transition state.

In a recent investigation of the silver ion assisted solvolysis of a series of keto halides it was observed that phenacyl chloride underwent solvolysis 1.3 times as fast as n-butyl chloride in 80% aqueous ethanol at 56° and that the activation enthalpy and entropy for phenacyl chloride differed substantially from what might have been expected in comparison with the values obtained for the higher homologs.[2] In view of the mechanistic implications of this earlier finding we have investigated more extensively the unassisted solvolysis[3] and the silver ion assisted solvolysis of phenacyl halides.

The procedure used for following the kinetics of the silver ion assisted solvolyses is identical with the procedure used in our earlier investigation[2] utilizing silver perchlorate as the source of the silver ion. Under these conditions clean second-order kinetics are observed.[2] The products derived from the silver ion assisted solvolysis of the phenacyl halides are only ethyl phenacyl ether and phenacyl alcohol; no rearrangement products, ethyl phenylacetate or phenylacetic acid, were observed. In all cases the predominant product was the ethyl phenacyl ether (~70%).[4]

The second-order rate constants for the silver ion assisted solvolysis of phenacyl chloride, bromide, and iodide are presented in Table I. The activation enthalpies and entropies as determined from the rate data are presented in Table II.

It is interesting to compare the trends in the rates of the unassisted and silver ion assisted solvolysis reactions. It was originally reported that phenacyl chloride undergoes silver ion assisted solvolysis at a rate 1.3 times that of n-butyl chloride in 80% ethanol at 56.2°.[2] Comparison of the calculated rate for the silver ion assisted solvolysis of phenacyl bromide in 70% ethanol at 64° (see Table III) reveals that phenacyl bromide solvolyzes somewhat slower in the presence of silver perchlorate than straight-chain alkyl

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE SILVER ION ASSISTED SOLVOLYSIS OF PHENACYL HALIDES[a]

Substrate	Solvent	—$k_2 \times 10^3$, l. mole^{-1} min^{-1} at—		
		40°	55°	70°
Phenacyl chloride	80% ethanol	0.060	0.319	1.16[b]
Phenacyl bromide	50% ethanol	10.8	43.2	121
Phenacyl bromide	80% ethanol	12.7	...	153
Phenacyl bromide	95% ethanol	16.7	61.4	200
Phenacyl iodide	80% ethanol	160	436	1230
p-NO$_2$-phenacyl bromide	80% ethanol	...	...	176
p-Cl-phenacyl bromide	80% ethanol	...	...	169
m-CH$_3$O-phenacyl bromide	80% ethanol	...	...	171
p-CH$_3$O-phenacyl bromide	80% ethanol	...	...	170

[a] Probable experimental uncertainty ±4%. [b] k_2 at 80°; 3.27 × 10^3 l. mole^{-1} min^{-1}.

TABLE II

ACTIVATION PARAMETERS FOR THE SILVER ION ASSISTED SOLVOLYSIS OF PHENACYL BROMIDES IN AQUEOUS ETHANOL

Substrate	Solvent	$\Delta H^{\ddagger}$, kcal/mole[a]	$\Delta S^{\ddagger}$, eu[b]
Phenacyl chloride	80% ethanol	21.2	18.1
Phenacyl bromide	50% ethanol	15.7	25.2
Phenacyl bromide	80% ethanol	17.1	20.9
Phenacyl bromide	95% ethanol	16.9	20.8
Phenacyl iodide	80% ethanol	14.1	25.2

[a] Estimated precision, ±0.8 kcal/mole. [b] Estimated precision, ±1.6 eu.

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[1] Research supported by the National Science Foundation, Grant GP-4497.

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[4] In the previous article[3] it was shown that ethyl phenacyl ether and phenacyl alcohol slowly equilibrate in aqueous ethanol under the conditions of the kinetic experiments.

Table III

Rate Constants for the Unassisted and Silver Ion Assisted Solvolysis of Organic Bromides

	$k_1 \times 10^3$, $\text{sec}^{-1\,a}$	$k_2 \times 10^4$, l. $\text{mole}^{-1}\ \text{sec}^{-1\,b}$
Methyl bromide	0.35	62.5
Ethyl bromide	0.14	76.9
Isopropyl bromide	0.26	...
n-Propyl bromide	...	42.0
Isobutyl bromide	...	6.44
Phenacyl bromide	0.27[c]	16[d]

[a] Values for methyl, ethyl, and isopropyl bromides in 80% ethanol at 55° taken from L. C. Bateman, K. A. Cooper, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 925 (1940). [b] Values for methyl, ethyl, *n*-propyl, and isobutyl bromides in 70% ethanol in the presence of silver nitrate at 64° are taken from J. Dostrovsky and E. D. Hughes, *ibid.*, 169 (1946). [c] Reference 3. [d] Calculated from the present data.

bromides in the presence of silver nitrate.[5] The data for phenacyl bromide display the same general trend as phenacyl chloride.

The greater rate of the silver ion assisted solvolysis of ethyl bromide over methyl bromide can be attributed to a balance between increased carbonium ion character in the transition state (methyl stabilizing effect leading to rate enhancement) and a less important increase in the steric inhibition to nucleophilic attack (resulting in a rate decrease). In contrast, the unassisted solvolysis of ethyl bromide occurs 0.4 times as fast as methyl bromide which is consistent with a lesser degree of carbonium ion character, owing to the lack of electrophilic assistance by silver ion, and the steric hindrance to nucleophilic attack by solvent molecules. The observation that phenacyl bromide undergoes unassisted solvolysis approximately twice as fast as ethyl bromide (highly nucleophilic displacements by solvent), whereas the silver ion assisted solvolysis of phenacyl bromide appears to be slower than the similar solvolysis of ethyl bromide, is also consistent with increased carbonium ion character in the transition state for the assisted over the unassisted solvolysis. Increased carbonium ion character in the phenacyl bromide is energetically unfavorable owing to the adverse inductive effect of the benzoyl portion of the molecule leading to greater rate retardation.

Additional evidence in support of this view is provided by the substituent effects in substituted phenacyl bromides. The Hammett ρ value for the silver ion assisted solvolysis of substituted phenacyl bromides in 80% ethanol at 70° is effectively 0, the rate constants for the *p*-nitro, *p*-chloro, *p*-methoxy, *m*-methoxy, and the unsubstituted phenacyl bromides being equal within experimental limits. In comparison the ρ value for the unassisted solvolysis of substituted phenacyl bromides in 80% ethanol at 70° is +0.35. The +0.35 ρ value and the Grunwald–Winstein m values of 0.20 ± 0.01 for the same reaction indicate that the transition state for the unassisted solvolysis is a highly nucleophilic attack by solvent molecules on carbon with the displacement of bromide ion.[3] The 0 ρ value for the silver ion assisted solvolysis indicates a transition state which has more carbonium ion character than the transition state for the unassisted solvolysis. However, the extremely neutral ρ value indicates that the total carbonium ion character is exceedingly low and that the transition state for the silver ion assisted solvolysis is best described as a highly concerted process in which solvent molecules undergo a nucleophilic displacement of a silver ion complexed halogen ion. This view is fully consistent with the view of Kornblum that the reaction of alkyl halides with silver salts is best represented as a graded SN1–SN2 reaction,[7] the present being highly SN2 like and perhaps is best termed an "electrophilically (Lewis acid) assisted nucleophilic displacement."

The values for the activation enthalpy and entropy for the silver ion assisted solvolysis of phenacyl chloride in 80% ethanol reported in the present investigation differ substantially from the values reported earlier.[2,8] The present value of 21.2 kcal/mole for $\Delta H^{\neq}$ falls within the range of values found in our earlier work with related systems (19.5 ± 1.5 kcal/mole) and should be regarded as the more reliable value. The present data do not require invoking the formation of a solvent addition intermediate which undergoes solvolysis, or participation by the carbonyl oxygen or phenyl group although the latter two mechanisms may be operative in solvent systems of lower nucleophilicity or in appropriately substituted phenacyl systems. Work in this area is currently in progress.

The Role of Silver Ion in Silver Ion Assisted Solvolysis.—The role of the electrophilic catalyst, in this case silver ion, is considered to be a specific solvation effect which can reduce the energy of the dipolar transition state.[9] A quantitative description of the role of the electrophilic catalysis has not been previously possible owing to various kinetic complications. Assisted solvolyses employing silver nitrate as the source of the silver ion result in kinetic orders that may vary from second- to higher nonintegral kinetic orders in a variety of solvents.[10] Similar observations have been made utilizing silver perchlorate in benzene[11] and acetonitrile;[12] the kinetic order in acetonitrile in dilute solutions approaches 1 but increases to just over 2 as the silver perchlorate concentration approaches 0.3

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(5) The data in Table III are for reactions in which silver nitrate is the source of the silver ion in contrast to silver perchlorate in the present investigation. Pocker[6] finds that 2-octyl bromide reacts more slowly with silver perchlorate in acetonitrile than with silver nitrate in acetonitrile. This effect is attributed to anion intervention in the rate-determining step. It is difficult to predict the relative rates of reaction of silver perchlorate and silver nitrate with a common alkyl bromide under identical conditions. In aqueous ethanol both salts are extensively more dissociated; however, the inability to obtain good second-order kinetics with silver nitrate in aqueous ethanol does indicate some complications. In aqueous ethanol the solvent molecules act as the nucleophiles[2] instead of the nitrate ion with silver nitrate in acetonitrile or with silver perchlorate in acetonitrile. This effect would level out the nucleophilic sensitivity of the reaction and leave differences in the electrophilic reagent only. In the absence of the necessary rate data only qualitative comparisons will be made.

(6) Y. Pocker and D. N. Kevill, *J. Am. Chem. Soc.*, **87**, 4771 (1965).

(7) N. Kornblum, W. J. Jones, and D. E. Hardies, *ibid.*, **88**, 1704 (1966).

(8) The source of this discrepancy is not apparent in that no apparent errors have been found in the earlier work. The previous values were obtained from data at 25, 40, and 56.2° and considerable time was required to complete a kinetic run thus increasing the possibility of random errors. The present temperature range of 40 to 80° along with higher concentrations of reactants resulted in considerably shorter times for completion, particularly at the higher temperatures. Arrhenius plots of the earlier and the present data were quite satisfactory.

(9) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 49.

(10) (a) I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 169 (1946); (b) H. Martin, *Compt. Rend.*, **232**, 1762 (1951); (c) C. Prevost, *ibid.*, **236**, 288 (1953); (d) C. Prevost and R. Boyer, *Bull. Soc. Chim. France*, 782 (1949); (e) C. Prevost and E. Singer, *ibid.*, 1068 (1950); (f) Y. Pocker and D. N. Kevill, *J. Am. Chem. Soc.*, **87**, 4760 (1965).

(11) M. F. Redies and T. Iredale, *J. Phys. Chem.*, **48**, 224 (1944).

(12) G. S. Hammond, M. F. Hawthorne, J. H. Waters, and B. M. Graybill, *J. Am. Chem. Soc.*, **82**, 704 (1960).

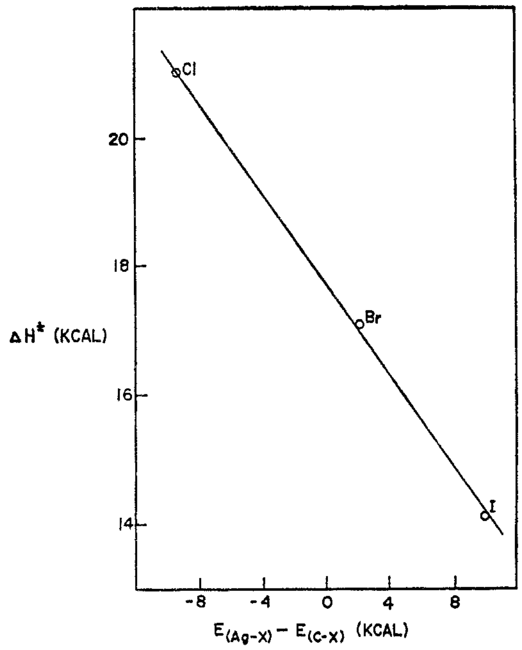

Figure 1.

M.[6] These complexities appear to be due to the association of the silver ion with the counterions in solution[10f,12,13] and the requirement that the counteranion also act as the nucleophile. In contrast to these results, the silver ion assisted solvolysis in aqueous ethanol follows clean, second-order kinetics,[2,3,14] first order each in alkyl halide and silver perchlorate.[15]

In previous studies using silver nitrate it has been reported that the precipitated silver halide is itself a catalyst for the reactions of alkyl halides; however, in our work,[2,3] and that of Pocker,[10f] such catalysis was not a serious factor.

As the present data appear to be free of the complications previously associated with electrophilic catalysts and with the availability of kinetic data for three halide systems in which the transition state is reasonably well defined from Hammett ρ and solvent effect data, it should be possible to make a meaningful correlation between the activation parameters and some measure of the role that the silver ion plays.

The role of the silver ion might be expected to vary as the S$_N$1 or S$_N$2 character of the transition state varies. In cases of highly S$_N$1-type transition states the role of the electrophilic catalyst might be expected to be minimal, the greatest contribution to $\Delta H^{\pm}$ arising from the carbon–halogen bond strength with the acceleration being primarily due to the reaction of silver ion with the halide ion in the tight ion or solvent-separated ion pairs. The effect of the electrophilic catalyst would be expected to be greatest in the highly concerted S$_N$2-assisted displacements.

A reaction typifying the latter category is the silver ion assisted solvolysis of the phenacyl halides. The transition state for this reaction must involve the formation and breaking of three bonds: the formation of the carbon–oxygen and silver–halogen bonds and the breaking of the carbon–halogen bond. If we assume that the carbon–oxygen bond formation occurs to the same extent with all three halides then only contributions from the carbon–halogen bond cleavage and silver–halogen bond formation need be considered. The activation enthalpies do not provide a linear correlation with either the carbon–halogen[16] or silver–halogen[17] bond energies alone. However, an excellent linear plot is obtained when $\Delta H^{\pm}$ is plotted *vs.* $E_{\text{CX}} - E_{\text{AgX}}$ (see Figure 1). The excellent linearity is undoubtedly fortuitous in that the same extents of bond cleavage and formation in the three transitions are not likely, and that exact values for the carbon–halogen bond energies in the phenacyl halides were not available.[16] Nonetheless the results indicate that electrophilic catalysis by silver ion in the phenacyl halide system leads to a transition state in which considerable carbon–halogen bond cleavage and silver–halogen bond formation, as well as carbon–oxygen bond formation, is occurring.

Experimental Section

Preparation of Starting Materials.—Phenacyl chloride and bromide were purified by repeated recrystallization from hexane. Phenacyl iodide was prepared by treatment of 15.5 g (0.1 mole) of phenacyl chloride with 15.8 g (0.105 mole) of sodium iodide in 70 ml of anhydrous acetone at room temperature for 4 hr. The reaction mixture was filtered to remove the precipitated sodium chloride and the acetone was rapidly removed under reduced pressure. The residue was dissolved in ether and washed with sodium thiosulfate to remove the free iodine. The resulting ether solution was dried over magnesium sulfate. Removal of the solvent gave a bright yellow oil which was repeatedly recrystallized from hexane giving colorless needles, mp 35° (lit.[18] mp 34.4°). Solutions of silver perchlorate were prepared by dissolving anhydrous silver perchlorate in aqueous ethanol. The solutions were filtered using a Celite filtration pad. The concentration of the silver perchlorate was determined by the Mohr method. The aqueous ethanol solvent systems were prepared from freshly distilled water (from permanganate) and 95% ethanol and standardized at 15.6°.

Kinetic Procedure.—Aliquots of standardized aqueous ethanol solutions of silver perchlorate and phenacyl halide (prepared by direct weighing procedures) were mixed in ampoules. The ampoules were sealed, wrapped in aluminum foil, and placed in the appropriate constant-temperature bath. The initial concentrations of the reactants were 0.02–0.05 mole l.$^{-1}$ of silver perchlorate with 0.012–0.033 mole l.$^{-1}$ phenacyl bromide or iodide and 0.11–0.195 mole l.$^{-1}$ of silver perchlorate with 0.10–0.19 mole l.$^{-1}$ of phenacyl chloride. Ampoules were periodically removed from the constant-temperature baths and the contents of the ampoules were washed into a beaker containing 25–30 ml of water. The perchloric acid in the sample was then titrated with standardized aqueous sodium hydroxide employing a Beckman Research Model pH meter equipped with standard calomel and glass electrodes.

Product Analyses.—Approximately 1 M solutions of silver perchlorate and the phenacyl halide were sealed in ampoules and maintained at the kinetic temperatures for several hours or days depending on the rate of the reaction. The contents of the ampoules were dissolved in ether. The ether solutions were washed once with a small volume of 5% sodium hydroxide to remove acidic products. The remaining ether solutions were dried over magnesium sulfate. After filtration and removal of the solvent, the residues were analyzed by gas–liquid partition

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[13] G. O. Parfitt and A. L. Smith, *Trans. Faraday Soc.*, **59**, 257 (1963).

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[15] Silver perchlorate is approximately five times more dissociated in acetonitrile than is silver nitrate at 25[10f] and hence would be expected to be more dissociated in aqueous ethanol $[K_{\text{dissoc}}(\text{AgNO}_3 \text{ in acetonitrile})/K_{\text{dissoc}}(70\% \text{ ethanol}) \approx 0.07]$.[10f,13]

[16] The carbon–halogen bond strengths for the phenacyl halides do not appear to be known. The values for the bond energies used in the present study are 81 kcal for CCl, 68 kcal for CBr, and 51 kcal for CI: T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Academic Press Inc., New York, N. Y., 1958.

[17] The silver–halogen bond strengths used are 71.7 kcal for AgCl, 70.2 kcal for AgBr, and 61.2 kcal for AgI: T. L. Allen, *J. Chem. Phys.*, **26**, 1644 (1957).

[18] H. Rheinholt and M. Perrier, *J. Am. Chem. Soc.*, **69**, 3148 (1947).

chromatography (glpc) on a 4-ft THEED on Chromosorb W column at 110° showing the presence of only phenacyl alcohol and ethyl phenacyl ether (approximately 30:70 ratio) and several very minor (unidentified) fractions. No ethyl phenylacetate was present in the neutral fraction.

The sodium hydroxide extracts (from above) were acidified and extracted with ether. The ether solutions were treated with small portions of ethereal diazoethane. The solvent was removed and the residues (approximately 5% by weight) were analyzed by glpc. No ethyl phenylacetate was present. Total recoveries of products averaged 90–95%.

Registry No.—Phenacyl chloride, 532-27-4; phenacyl bromide, 70-11-1; phenacyl iodide, 00-00-0; p-NO_2-phenacyl bromide, 99-81-0; p-Cl-phenacyl bromide, 536-38-9; m-CH_3O-phenacyl bromide, 000-00-0; p-CH_3O-phenacyl bromide, 2632-13-5.

Group Contributions to Phosphorus-31 Chemical Shifts of Tertiary Phosphines

SAMUEL O. GRIM, WILLIAM MCFARLANE, AND EDWARD F. DAVIDOFF

Department of Chemistry, University of Maryland, College Park, Maryland 20740

Received October 20, 1966

Additive alkyl group contributions to the phosphorus-31 chemical shifts of tertiary phosphines have been assigned for 12 alkyl groups. These group contributions are shown to be related to the number of carbon substituents on the α and β positions of the alkyl groups. Previously unreported phosphorus-31 chemical shift data are also presented for some tertiary phosphines.

The idea of additive group contributions to the phosphorus-31 chemical shifts in trivalent phosphorus compounds was first suggested in 1956 by Van Wazer[1] and co-workers. This concept has been criticized favorably and unfavorably since then and much of the discussion, ranging from simple empiricism to quantum mechanics, has been concerned with the magnitude and sign of the chemical shifts.[2–9] There seems to be general agreement that bond angles and electronegativities of the groups are major factors in determining the ^{31}P chemical shift, while other factors such as the effect of the lone-pair excitation energy and π bonding are not well agreed upon. One remarkable paper[10] proposes that the ^{31}P chemical shift in trivalent phosphorus compounds depends only on bond angles and "magnetic configuration" of the molecule. This same idea extended to quadruply bonded phosphorus compounds implies that all tetraorganophosphonium salts, *i.e.*, tetraphenyl-, tetramethyl-, and tetrabutylphosphonium, would have the same ^{31}P chemical shift. This is not the case.[11]

Most of the reports have attempted to treat all types of PZ_3 (Z = alkyl, aryl, alkoxy, halogen, hydrogen, etc.) compounds, but we are concerned in this work with only trialkyl-, dialkylphenyl-, and alkyldiphenylphosphines, which have previously been treated by both quantum mechanical[9] and empirical procedures.[3,4]

In previous work it was noted that the order of group contributions is Me > Et > i-Pr > t-Bu in tertiary, secondary, and primary phosphines and in quaternary phosphonium salts (part of the series was also reported for phosphonates[1]). This is the reverse order of the inductive effect as one would have normally expected the t-butyl to shield phosphorus most in this series, and hence result in the highest ^{31}P chemical shift and the largest group contribution. The experimental series might be explained in several ways. (a) Alkyl groups are more electronegative than phosphorus in phosphines and hence t-butyl can accept more electronic change than isopropyl, etc. (it is well known that, if Z is more electronegative than R in RZ compounds, the electronegativity series is Me > Et > i-Pr > t-Bu, and it has also been shown that, if R is more electronegative than Z, the electronegative series is t-Bu > i-Pr > Et > Me).[12] However, the electronegativity argument probably loses its cogency within a series of alkyl groups which all lie very close together in electronegativities and, indeed, very close to the electronegativity of phosphorus itself. Huheey[13] has calculated that the electronegativities of the alkyl groups in this study lie between 2.34 and 2.39 and that a phosphorus hybrid p orbital which contains 13.7% s character (based on the observed bond angle in trimethylphosphine) has an electronegativity of 2.38. If three or four significant figures in electronegativity values can be reliable (which we doubt), then perhaps electronegativity arguments could be applied to this problem. (b) As the alkyl group becomes larger the bond angles increase and the phosphorus bonds gain s character with concomitant increase in the p character of the lone pair. Assuming that a lone pair is more effective in shielding the nucleus than bonding pairs, a lone pair with large s character would be most effective in shielding because of its spherical symmetry about the nucleus. Thus small alkyl groups (small bond angles, large s character of the lone pair, high shielding) should have large group contributions. (c) Hyperconjugation of the α protons could occur, $R_2\ddot{P}CR_2H \leftrightarrow R_2\underset{-}{\ddot{P}} = CR_2\ \underset{+}{H}$, leading to the most shielding of phosphorus by those alkyl groups with the largest number of α protons. This type of hyperconjugation has been sug-

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