eluent. The first fraction collected off the column contained 204 mg (41%) of a light yellow oil whose structure was identified as 2-[(5-butenyl)carboxy]-3-phenyl-2*H*-azirine (**35**): NMR (CCl_4, 90 MHz) δ 2.03 (dd, 2 H, J = 6.6, 1.0 Hz), 2.37 (s, 1 H), 3.83 (t, 2 H, J = 6.6 Hz), 4.61–4.89 (m, 2 H), 5.21–5.36 (m, 1 H), 7.16–7.36 (m, 3 H), 7.50–8.66 (m, 2 H); IR (neat) 3080, 2980, 1820, 1765, 1727, 1625, 1445, 1330, 1238, 1185, 1012, 755 cm^{-1}; MS, m/e 215, 174, 165, 161, 116; UV (cyclohexane) 238 nm (ϵ 9000). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.29; H, 5.98; N, 6.41.

The second fraction isolated contained a colorless oil that crystallized in a 25% ethyl acetate/hexane mixture to afford 167 mg (34%) of a white crystalline solid (mp 74–75 °C) whose structure was identified as 3-aza-1,6-dioxa-2-phenyltricyclo-[3.5.0^{5,9}]dec-2-ene (**36**): NMR (C_6D_6, 90 MHz) δ 1.10 (dtd, 1 H, J = 13.2, 6.5, 4.2 Hz), 1.50 (ddd, 1 H, J = 13.2, 6.5, 5.4 Hz), 1.75 (ddd, 1 H, J = 13.2, 6.5, 2.7 Hz), 1.92 (ddd, 1 H, J = 13.2, 9.0, 3.0 Hz), 2.75 (dddd, 1 H, J = 9.0, 7.8, 5.4, 4.2 Hz), 3.67 (dt, 1 H, J = 9.0, 6.5 Hz), 3.87 (dt, 1 H, J = 9.0, 6.5 Hz), 4.36 (ddd, 1 H, J = 6.5, 3.0, 1.2 Hz), 7.01–7.29 (m, 3 H), 8.16–8.40 (m, 2 H); IR (KBr) 3008, 2963, 2908, 1623, 1568, 1475, 1439, 1323, 1241, 1188, 1108, 1023, 974, 833 cm^{-1}; MS, m/e 178, 163, 144, 123, 119, 117; UV (cyclohexane) 242 nm (ϵ 11300). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.42; H, 6.08; N, 6.50.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health. A.P. thanks the organic faculty at the University of Wurzburg for their gracious hospitality during his stay at the Institute as an Alexander von Humboldt Senior Awardee. Use of the high-field NMR spectrometer used in these studies was made possible through a NSF equipment grant.

Registry No. **5**, 82238-43-5; **6**, 67909-78-8; **7**, 5014-83-5; **8**, 82238-48-0; **9**, 67909-83-5; **10**, 82301-27-7; **11**, 87696-38-6; **12**, 82238-44-6; **13**, 82238-45-7; **14**, 82238-49-1; **15**, 82238-50-4; **16**, 82238-47-9; **17**, 62762-73-6; **18**, 82238-52-6; **20**, 82238-46-8; **21**, 82238-51-5; **22**, 82238-38-8; **23**, 87696-39-7; **24**, 87696-40-0; **25**, 87696-41-1; **26**, 5014-83-5; **27**, 87696-43-3; **28**, 87696-42-2; **29**, 87696-44-4; **30**, 7449-60-7; **31**, 20662-94-6; **32**, 87696-46-6; **33**, 87696-47-7; **34**, 87696-49-9; **35**, 87696-50-2; **36**, 87696-51-3; CH_2=$CHCH_2Br$, 106-95-6; $PhCONHCH_2CO_2(CH_2)_4CH$=CH_2, 87696-45-5; $PhCONHCH_2CO_2(CH_2)_2CH$=CH_2, 87696-48-8; 2-chloro-4,5-diphenyloxazole, 49656-04-4; allyl alcohol, 107-18-6; benzyl alcohol, 100-51-6; crotyl alcohol, 6117-91-5; 3-methyl-2-butenol, 556-82-1; furfuryl alcohol, 98-00-0; 4,5-diphenyl-2-methyloxazole, 14224-99-8; 1-bromo-4-pentene, 1119-51-3; hippuric acid, 495-69-2; 5-hexen-1-ol, 821-41-0; 3-buten-1-ol, 627-27-0.

Phosphazenes. 4. Synthesis and Spectral Characteristics of a Series of 1-Aryl-1-alkyltetrachlorocyclotriphosphazenes[1]

Paul J. Harris,* Kenneth B. Williams, and Bernie L. Fisher

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0699

Received July 26, 1983

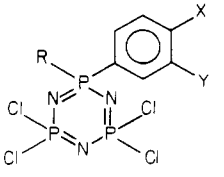
A new series of 1-aryl-1-alkyltetrachlorocyclotriphosphazenes has been synthesized. These compounds, which contain various substituents in the meta and para positions of the aryl group, have been characterized by infrared and NMR (^1H, ^{13}C, ^{19}F, and ^{31}P) spectroscopy and mass spectrometry. The ^1H and ^{13}C NMR spectra can be used to obtain a value for the Hammett σ_{para} parameter of 0.63 for the $N_3P_3Cl_4CH_3$ group, while ^{19}F NMR can be used to obtain Taft reactivity parameters of σ_I = 0.48 and σ_R = 0.16. These values are very similar to those found for a cyano group, and the similarity of the electron-withdrawing power between the $N_3P_3Cl_4CH_3$ and cyano groups is confirmed by a study of the ultraviolet spectra of the new aryl compounds.

Introduction

Over the past several years, the nature of the electronic interactions between a phosphazene ring and various exocyclic substituents has been the subject of much controversy.[2-10] Aryl-substituted phosphazenes have been subjected to examination by a wide variety of techniques, such as ultraviolet–visible spectroscopy,[3] nuclear magnetic resonance spectroscopy utilizing nuclei such as ^1H,[4] ^{13}C,[5] ^{19}F,[6] and ^{31}P,[7] electron-spin resonance spectroscopy,[8] nuclear quadrupole resonance spectroscopy observing ^{35}Cl nuclei,[9] and, finally, photoelectron spectroscopy.[10] The results of these various studies have been interpreted as indicating no,[10] little,[3,5,7] or extensive[2,4,6] resonance interactions between the aryl substituent and the phosphazene ring.

However, all of these studies to date have been limited to simple aryl- or fluoroaryl-substituted phosphazenes. This is due, in no small part, to the problems involved in the synthesis of spectroscopically instructive aryl-substituted phosphazene compounds.

In this paper we describe the synthesis and spectral characteristics of a new series of para- and meta-substituted arylchlorophosphazenes of general structure I. This



I

R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9; X = Y = H
R = CH_3; Y = H, X = $N(C_2H_5)_2$, $N(CH_3)_2$, OCH_3, t-C_4H_9, CH_3, C_6H_5, F, Cl, CF_3
R = CH_3; X = H; Y = $N(CH_3)_2$, OCH_3, F

is the first time that such a wide variety of aryl-substituted phosphazene compounds has been synthesized. These

(1) For part 3, see: Harris, P. J. *Inorg. Chim. Acta* **1983**, *71*, 233.
(2) Gallicano, K. D.; Oakley, R. T.; Sharma, R. D.; Paddock, N. L. "Proceedings of the 1981 International Conference on Phosphorus Chemistry" (*ACS Symp. Ser. no. 171*); American Chemical Society: Washington, D.C. 1981, p 301.
(3) Wagner, A. J.; Moeller, T. *J. Inorg. Nucl. Chem.* **1971**, *33*, 1307.
(4) Allen, C. W.; White, A. J. *Inorg. Chem.* **1974**, *13*, 1220.
(5) Allen, C. W. *J. Organomet. Chem.* **1977**, *125*, 215.
(6) Chivers, T.; Paddock, N. L. *Inorg. Chem.* **1972**, 11, 848.
(7) Allen, C. W.; Moeller, T. *Inorg. Chem.* **1968**, *7*, 2177.
(8) Allcock, H. R.; Birdsall, W. J. *Inorg. Chem.* **1971**, *10*, 2495.
(9) Whitehead, M. A. *Can. J. Chem.* **1964**, *42*, 1212.
(10) Allen, C. W.; Green, J. C. *Inorg. Chem.* **1980**, *19*, 1719.

0022-3263/84/1949-0406$01.50/0

Table I. Arylalkylphosphazenes Characterization Data

compound	% yield	mp or bp (mm), °C
$N_3P_3Cl_4(CH_3)(C_6H_5)$	76	76-78
$N_3P_3Cl_4(C_2H_5)(C_6H_5)$	43	106 (0.1)
$N_3P_3Cl_4(n\text{-}C_3H_7)(C_6H_5)$	35	120 (0.1)
$N_3P_3Cl_4(n\text{-}C_4H_9)(C_6H_5)$	24	125 (0.1)
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4N(CH_3)_2)$	35	130
$N_3P_3Cl_4(CH_3)(m\text{-}C_6H_4N(CH_3)_2)$	21	150 (0.1)
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4N(C_2H_5)_2)$	26	96-98
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4OCH_3)$	46	73
$N_3P_3Cl_4(CH_3)(m\text{-}C_6H_4OCH_3)$	18	145 (0.1)
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4\text{-}t\text{-}C_4H_9)$	58	141
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4CH_3)$	50	66-69
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4C_6H_5)$	17	81-83
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4F)$	24	58-60
$N_3P_3Cl_4(CH_3)(m\text{-}C_6H_4F)$	18	62
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4Cl)$	20	70-75
$N_3P_3Cl_4(CH_3)(p\text{-}C_6H_4CF_3)$	32	98

molecules provide an excellent probe for the electronic interactions between the chlorophosphazene ring and the aryl substituent.

This work was initiated in order to answer the following questions: (1) Could a large and spectroscopically instructive series of aryl-substituted phosphazenes be synthesized? (2) Is it possible to classify the chlorophosphazene group with other "standard" aromatic substituents with regard to its electron-donating or -withdrawing power toward the benzene ring? (3) What is the nature and extent of the electronic interactions between the aryl group and the chlorophosphazene?

Results and Discussion

Synthesis and Characterization of Arylalkylphosphazenes. The synthesis of aryl-substituted phosphazenes from hexachlorocyclotriphosphazene has been successful in only a few limited cases.[11] Indeed, attempts to synthesize aryl-substituted phosphazenes by the reactions between hexachlorocyclotriphosphazene and aryl Grignard reagents have recently been shown to yield ring-coupled phosphazenes and very few substituted products.[12,13] However, other studies on the reactions between methylpentachlorocyclotriphosphazene and various amines or alkoxides indicated that the halogen atom geminal to the methyl group could be readily, and exclusively, substituted,[14] and it was with this compound that we chose to initiate this study.

The reaction between methylpentachlorocyclotriphosphazene and phenylmagnesium bromide led to a good yield of the 1-phenyl-1-methyl-substituted compound, I (R = CH_3; X = Y = H). Following the success of this reaction, the synthetic scheme was extended to other aryl Grignard reagents. These reactions also proved successful and led to the isolation of a wide variety of arylalkylphosphazenes of general structure I. Yields for all of the reactions are listed in Table I.

The molecular structure of these new compounds was determined by the use of a combination of ^1H and ^{31}P NMR, infrared, and ultraviolet spectroscopy, mass spectrometry, and, in representative cases, elemental microanalysis. General characterization data for all new compounds are listed in Table I. Nuclear magnetic resonance data are listed in Table II and ultraviolet and mass spectral data are listed in Table III. (Tables II and III are available as supplementary material.) The retention of the phosphazene ring in compound I was confirmed by infrared and ^{31}P NMR spectroscopy. The infrared spectra showed intense absorbances between 1100 and 1300 cm^{-1}, a characteristic of the PN skeleton in cyclic phosphazene compounds.[15] The geminal substitution pattern of the phosphazene ring was confirmed by both ^1H and ^{31}P NMR spectroscopy. The ^1H NMR spectrum always showed the resonance for the P-CH_3 group as a doublet of triplets centered at δ ~1.8. This is shifted upfield from the resonance for the methylpentachlorophosphazene compound, which is found at δ 2.1.[14] The ^{31}P NMR spectrum (^1H decoupled) in all cases was interpreted as an AB_2 spin system.[15] The PCl_2 resonance always occurred at ~18.5 ppm, as a doublet, while the P(aryl)(alkyl) resonance appeared as a triplet, centered between 30.0 and 27.7 ppm. This resonance broadened significantly upon ^1H coupling. For the para-substituted aryl compounds, this resonance was found to shift in a manner that was found to be directly proportional to the Hammett σ constants for the various para substituents.[16,17] These results have been discussed elsewhere.[1]

Chlorophosphazene as an Aryl Substituent. In order to place the chlorophosphazene ring in a scale with other "standard" aromatic substituents, an examination of the ^1H[4], ^{13}C[5], and ^{19}F[6] NMR spectra of several of the new aryl compounds was performed. The NMR chemical shifts of para proton,[18,19] carbon,[18-20] and fluorine[19,21] nuclei have been used in many cases to quantify the nature of the interaction between a substituent and an aromatic ring, although in some cases it is difficult to separate the inductive and resonance contributions to the NMR chemical shift.[21,22] All three of these techniques have been used to probe the substituent effect of the fluorophosphazene group, and in all cases this substituent was found to be similar to the nitro group in terms of its electron-withdrawing power.[4-6]

The ^1H NMR spectrum of compound I (R = CH_3; X = Y = H) showed the resonance for the para hydrogen at δ 7.51, while the para carbon resonance for this compound was observed at 132.45 ppm. Both these chemical-shift values are similar to that observed for benzonitrile[23] and indicate that the chlorophosphazene ring exerts a moderately strong electron-withdrawing effect on the benzene ring. A comparison of both these chemical shifts with plots of chemical shift vs. the Hammett σ_{para} constants for various aryl substitutents[18] gave a value for the Hammett σ_{para} parameter for the chlorophosphazene of 0.61 (^{13}C) and 0.65 (^1H) (average σ_{para} = 0.63). This value is similar to that determined for the cyano group [σ_{para} (CN) = 0.628].[16]

Nature of the Phosphazene–Aryl Interaction. Although it is relatively simple to obtain a value for the Hammett σ_{para} parameter for the phosphazene ring from the ^1H and ^{13}C NMR data, this value gives no information as to the degree of inductive or resonance interactions between the phosphazene ring and the aryl group. This

(11) Acock, K. G.; Shaw, R. A.; Wells, F. B. G. *J. Chem. Soc.* **1964**, 121.
(12) Harris, P. J.; Desorcie, J. L.; Allcock, H. R. *J. Chem. Soc., Chem. Commun.*, **1981**, 852.
(13) Allcock, H. R.; Desorcie, J. L.; Harris, P. J. *J. Am. Chem. Soc.* **1983**, *104*, 2482.
(14) Allcock, H. R.; Harris, P. J. *Inorg. Chem.* **1981**, *20*, 2844.
(15) Allcock, H. R.; Harris, P. J.; Connolly, M. S. *Inorg. Chem.* **1981**, *20*, 11.
(16) March, J. "Advanced Organic Chemistry; Reactions, Mechanisms and Structure", 2nd ed.; McGraw Hill: New York, 1977.
(17) Hammett, L. P. *J. Am. Chem. Soc.* **1937**, *59*, 96.
(18) Spiesecke, H.; Schneider, W. G. *J. Chem. Phys.* **1961**, *35*, 731.
(19) Wu, T. K.; Dailey, B. P. *J. Chem. Phys.* **1964**, *41*, 2796.
(20) Nelson, G. L.; Levy, G. C.; Cargioli, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 3089.
(21) Adcock, W.; Gupta, B. D. *J. Am. Chem. Soc.* **1975**, 6871.
(22) Adcock, W.; Khor, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7799.
(23) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed., Wiley: New York, 1981.

information is typically displayed by the Taft σ_I and σ_R constants, where $\sigma = \sigma_I + \sigma_R$.[24] For many groups, this information has been obtained by inspection of the ^{13}C NMR spectra[25] or of the ^{19}F NMR data for *m*- and *p*-fluorophenyl-substituted derivatives.[6,19,26-28] The variation of the ^{19}F NMR chemical shifts with the π electron density in the aryl group have been justified theoretically,[29-31] and the shielding parameters correlated with the Taft reactivity parameters σ_I and σ_R.[6,27] In order to obtain these Taft values for the chlorophosphazene ring, an investigation of the ^{19}F NMR of compounds I (R = CH_3, X = H, Y = F or X = F, Y = H) was carried out. These data are listed in Table II. The shielding parameter, $\int_H^{para\text{-}X}$, for the para compound, I (R = CH_3; X = F; Y = H) was found to be −7.49, while that for the meta compound, I (R = CH_3; X = H; Y = F), $\int_H^{meta\text{-}X}$, was found to be −2.84.[32] From these data, values for the Taft reactivity constants of σ_I = +0.48 and σ_R = +0.16 can be obtained[33] and are confirmed by the ^{13}C NMR data. These values are again similar to those derived for the cyano group[6,26] (σ_I = +0.48, σ_R = +0.21) and indicate that the inductive withdrawing power of the chlorophosphazene ring is comparable to the cyano group, while the resonance interaction appears to be slightly less. However, the magnitude of the σ_R value for the phosphazene ring compares favorably with that determined for other phosphorus groups.[28]

Ultraviolet Spectra. In a further attempt to probe the resonance interactions between the phosphazene ring and the aryl substituent, it was decided to investigate the ultraviolet spectra of the new phosphazene compounds. These data are listed in Table III. In each case, the ultraviolet spectrum shows an absorption band similar to that observed for other arylphosphazene compounds[3] and para-disubstituted aromatics.[34] It is known that in aromatic compounds in which a resonance donor and a resonance acceptor group are para to each other, the ultraviolet spectrum is shifted to longer wavelength when compared to similarly substituted meta compounds.[23,34-36]

For the compounds I (R = CH_3, X = H, Y = $N(CH_3)_2$, or X = $N(CH_3)_2$, Y = H), differences are found in the ultraviolet spectra between the para and the meta compounds,[37] $\delta\lambda_{max}^{N(CH_3)_2} = 17$. For the methoxy compounds I (R = CH_3, X = H, Y = OCH_3 or X = OCH_3, Y = H), $\delta\lambda_{max}^{OCH_3} = 8$. If these values are compared to that obtained for amino-[38,39] or methoxybenzonitrile[40] ($\delta\lambda_{max}^{N(CH_3)_2} = 25$; $\sigma\lambda_{max}^{OCH_3} = 25$), it is clear that the degree of resonance interaction between the phosphazene and the aryl group is less than the nitrile–aryl interaction. This is in complete agreement with the information derived from the NMR studies.

Conclusion

It is clear from both the NMR and UV studies that the phosphazene ring exerts a moderately strong electron-withdrawing effect upon the benzene ring. From the ^1H and ^{13}C NMR data, a value of the Hammett σ_{para} parameter of 0.63 was obtained, and this is very similar to that of the cyano group. Consideration of the ^{19}F NMR data of the m- and *p*-fluoro compounds gave values for the Taft reactivity parameters σ_I of 0.48 and σ_R and 0.16 respectively, which indicated that ~75% of the electron withdrawal by the phosphazene ring is by an inductive mechanism. These results were confirmed by an ultraviolet study of the new compounds.

Experimental Section

Hexachlorocyclotriphosphazene was purchased from Aldrich Chemical Co. or Alfa-Ventron Corp. and was purified by vacuum sublimation (60 °C, 0.1 mm), followed by successive recrystallizations from *n*-hexane until a melting point of 112 °C was obtained. The organometallic reagents and aryl halides were also purchased from Aldrich Chemical Co. or Alfa-Ventron Corp. *m*-Bromo-*N*,*N*-dimethylaniline was synthesized from *m*-bromoaniline by standard procedures.[41] All aryl halides were distilled before use. Tetrahydrofuran (THF) was dried over a sodium–benzophenone ketyl mixture and was distilled into the reaction flask under an atmosphere of dry nitrogen. Hexane was dried and distilled over calcium hydride while dichloromethane was dried over P_4O_{10}. All of the reactions described in this work were performed under an atmosphere of dry nitrogen. Methylpentachlorocyclotriphosphazene[14] and the Grignard reagents were prepared by standard procedures. The Grignard reagents were standardized by titration (performed under an atmosphere of dry nitrogen) with 1.0 M *sec*-butyl alcohol in toluene. The indicator used was 1,10-phenanthroline hydrate.[42]

Nuclear magnetic resonance spectra were obtained with the use of a Perkin-Elmer EM 390 spectrometer (^1H and ^{19}F) or a JEOL 200 spectrometer (^1H, ^{13}C, ^{31}P). All spectra were obtained on samples dissolved in $CDCl_3$. An internal standard of tetramethylsilane was used as the reference for the ^1H and ^{13}C spectra. The ^{19}F NMR spectra were referenced to internal CCl_3F, while ^{31}P NMR spectra were referenced to a capillary of 85% H_3PO_4 inserted into the sample.[1] Infrared spectra were obtained with the use of a Perkin-Elmer 710B spectrometer. The samples were prepared as KBr pellets. Ultraviolet spectra were obtained on a Hitachi Perkin-Elmer 100-60 spectrophotometer. The samples were dissolved in either hexane or methanol. Beer's law plots were obtained by successive dilutions of a standard stock solution (typically 10^{-4} M). Mass spectral data were obtained by the use of a Varian MAT 112 magnetic sector instrument operating at 70 eV.[43]

Synthesis of 1-Aryl-1-methyltetrachlorocyclotriphosphazenes (I). All of these compounds were prepared by an identical procedure. The following is a typical example: Methylpentachlorocyclotriphosphazene[14] (2.0g, 6.1 mmol) was dissolved in THF (~150 mL) and cooled to 0 °C. The phenylmagnesium bromide (18 mmol, solution in THF) was added dropwise over a period of 15 min, and the reaction mixture was then allowed to stir for 24 h at room temperature. The solvent was removed under vacuum and the crude product was dissolved in CH_2Cl_2 (50 mL). This solution was then filtered through neutral alumina, and the solvent was again removed under vacuum.

(24) Taft, Jr., R. W. "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13, pp 578–580 and 594–597.
(25) Brownlee, R. T. C.; Topsom, R. D. *Tetrahedron Lett.* **1972**, *51*, 5187.
(26) Taft, Jr., R. W. *J. Am. Chem. Soc.* **1957**, *79*, 1045.
(27) Taft, Jr., R. W.; Price, E.; Fox, I. R.; Lewis, I. C.; Andersen, K. K.; Davis, G. T. *J. Am. Chem. Soc.* **1963**, *85*, 3146.
(28) Rakshys, J. W.; Taft, Jr., R. W.; Sheppard, W. A. *J. Am. Chem. Soc.* **1968**, *90*, 5236.
(29) Karplus, M.; Das, T. P. *J. Chem. Phys.* **1961**, *34*, 1683.
(30) Prosser, F.; Goodman, L. *J. Chem. Phys.* **1963**, *38*, 374.
(31) Boden, N.; Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *Mol. Phys.* **1964**, *8*, 133.
(32) The shielding parameters, $\int_H^{para\text{-}X}$ or $\int_H^{meta\text{-}X}$ are simply the ^{19}F chemical-shift value for the compound relative to fluorobenzene. Negative values indicate a downfield shift.
(33) Calculated from the following equations:[6,25] $\lambda_I = 0.1409(0.6 - \int_H^{meta\text{-}X})$ and $\sigma_R = 0.0339(\int_H^{meta\text{-}X} - \int_H^{para\text{-}X})$.
(34) Doub, L.; Vandenbelt, J. M. *J. Am. Chem. Soc.* **1947**, *69*, 2714.
(35) Doub, L.; Vandenbelt, J. M. *J. Am. Chem. Soc.* **1949**, *71*, 2414.
(36) Corbett, J. F. *Spectrochim. Acta.* **1967**, *23A*, 2315.
(37) $\delta\lambda_{max}^R = \lambda_{max}^{para} - \lambda_{max}^{meta}$ for substituent R.
(38) "Organic Electronic Spectra"; Kamlet, M. J., Ed.; Interscience, New York, 1946; Vol. I.
(39) "Organic Electronic Spectra"; Ungnade, H. E., Ed.; Interscience: New York, 1953; Vol. II.
(40) "Organic Electronic Spectra"; Wheeler, O. H.; Kaplan, L. A., Eds.; Interscience: New York, 1956; Vol. III.
(41) Billman, J. H.; Radike, A.; Mundy, B. W. *J. Am. Chem. Soc.* **1942**, *64*, 2977.
(42) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.
(43) Harris, P. J.; Williams, K. B. *Org. Mass Spectrom.*, in press.
(44) Elemental analyses were performed by MultiChem Laboratories, Lowell, MA.

Finally, the product was dissolved in toluene (50 mL), and this solution was washed with aqueous HCl (50 mL, 10% solution; for the amine compounds, distilled water was used in the wash). The layers were then separated, and the organic layer was dried over $MgSO_4$. The solvent was removed under vacuum, and the product, 1-phenyl-1-methyltetrachlorocyclotriphosphazene, was recrystallized from *n*-hexane. Yields and mp/bp data are listed in Table I. The NMR data (^1H, ^{19}F, ^{31}P) are listed in Table II. Ultraviolet and mass spectral data are listed in Table III. Tables II and III are available as supplementary material.

Elemental Microanalytical Data.[44] Compound I (R = CH_3; X = Y = H): Anal. Calcd for $C_7H_8N_3P_3Cl_4$: C, 22.76; H, 2.17; N, 11.38; P, 25.20; Cl, 38.48. Found: C, 22.71; H, 2.30; N, 11.03; P, 24.73; Cl, 38.31.

Compound I (R = CH_3; Y = H; X = $N(CH_3)_2$): Anal. Calcd for $C_9H_{13}N_4P_3Cl_4$: C, 26.21; H, 3.16; N, 13.58; P, 22.57; Cl, 34.47. Found: C, 26.41; H, 3.41; N, 13.46; P, 22.19; Cl, 34.51.

Compound I (R = CH_3; Y = H; X = F): Anal. Calcd for $C_7H_7N_3P_3Cl_4F$: C, 21.71; H, 1.81; N, 10.85; P, 24.03; Cl, 36.69. Found: C, 21.79; H, 2.13; N, 10.68; P. 24.00; Cl, 36.38.

Compound I (R = CH_3, Y = H, X = CF_3). Anal. Calcd for $C_8H_7N_3P_3Cl_4F_3$: C, 21.97; H, 1.60; N, 9.61; P, 21.28; Cl, 32.49. Found: C, 21.36; H, 1.63; N, 9.44; P, 21.03; Cl, 32.29.

Acknowledgment. This research was supported by a grant from Research Corp.

Registry No. I (R = CH_3; X = Y = H), 84811-29-0; I (R = C_2H_5; X = Y = H), 86709-58-2; I (R = *n*-C_3H_7; X = Y = H), 86711-94-6; I (R = *n*-C_4H_9; X = Y = H), 86709-59-3; I (R = CH_3; X = $N(CH_3)_2$; Y = H), 87048-81-5; I (R = CH_3; X = H; Y = $N(CH_3)_2$), 87921-97-9; I (R = CH_3; X = $N(C_2H_5)_2$; Y = H), 87048-82-6; I (R = CH_3; X = OCH_3; Y = H), 87048-79-1; I (R = CH_3; X = H; Y = OCH_3), 87921-98-0; I (R = CH_3; X = *t*-C_4H_9; Y = H), 87048-84-8; I (R = CH_3; X = CH_3; Y = H), 87048-78-0; I (R = CH_3; X = C_6H_5; Y = H), 87048-83-7; I (R = CH_3; X = F; Y = H), 87048-77-9; I (R = CH_3; X = H; Y = F), 87921-99-1; I (R = CH_3; X = Cl; Y = H), 87048-76-8; I (R = CH_3; X = CF_3; Y = H), 87048-80-4; methylpentachlorocyclotriphosphazene, 71332-21-3; phenyl bromide, 108-86-1.

Supplementary Material Available: NMR data (Table II) and UV and mass spectral data (Table III) of arylalkylphosphazines (17 pages). Ordering information is given on any current masthead page.

Carbon-13 Nuclear Magnetic Resonance Studies of Carbocations. 10.[1] Variation of Cationic Carbon Chemical Shifts with Increasing Electron Demand in 1,1-Diaryl-1-methyl (Benzhydryl) Carbocations

David P. Kelly* and Margot J. Jenkins

Department of Organic Chemistry, University of Melbourne, Parkville, Victoria, Australia 3052

Received June 23, 1983

A series of 28 1-X-phenyl-1-Z-phenyl-1-methyl (benzhydryl) carbocations, where the X and Z substituents have been varied over the range of electron demand (3,4-CH_2CH_2O, **11**; 4-OCH_3, **12**; 4-CH_3, **13**; 4-F, **14**; 4-H, **1**; 4-CF_3, **15**; 3,5-$(CF_3)_2$, **16**), have been prepared from the corresponding alcohols by ionization in superacids and their ^{13}C NMR spectra recorded at low temperatures (−70 to −10 °C). Plots of the substituent chemical shifts of the cationic carbons ($\Delta\delta C^+$) at −70 °C against σ^{C^+} are linear for the electron donors (Z = 3,4-CH_2CH_2O to Z = H) of **13**–**16** and **1** but deviate upward from this correlation line (relative shielding) for the electron acceptors (Z = H to Z = 3,5-$(CF_3)_2$). The plots of the highly stabilized cations **11** and **12** approximate shallow curves where groups more electron demanding than 4-CH_3 cause relative *shielding* of the cationic carbon. All these plots are interpreted in terms of competing resonance and localized inductive π-polarization effects.

Previous ^{13}C NMR studies of 4-substituted benzhydryl cations **1** in (Chart I) in superacids indicated that while the chemical shifts of the para carbon in the unsubstituted ring ($\delta C_{4'}$) correlated well with Hammett–Brown σ^+ constants derived from solvolysis, those of the cationic carbons did not.[2] A subsequent investigation of 2-phenylpropyl (cumyl) cations **3** revealed a major deviation from linearity in the plot of cationic carbon substituent chemical shifts ($\Delta\delta C^+$) against σ^+.[3] This led to the development of σ^{C^+} constants[4] which have now been shown to correlate the cationic carbon shifts of a wide range of acyclic,[5,6] cyclic,[7,8] and multicyclic cations.[6,9]

However, 2-aryl-2-norbornyl (**4**),[10-12] 3-aryl-3-nortricyclyl (**5**),[10,12] 1-aryl-1-cyclopropylethyl (**6**)[10] and 1,1-diaryl-1-ethyl (**2**)[10,11] cations showed deviations in the plots of $\Delta\delta C^+$ against electron demand (either σ^{C^+} or δC^+ of 1-aryl-1-cyclopentyl cations[4,11,12]) such that the cationic carbons of those cations with substituents more electron demanding then *p*-H, were more shielded than that predicted by the correlation line for the (π) electron donors.[10] These deviations were interpreted in terms of three different effects, the onset of nonclassical σ bridging,[11-13] the onset of increased cyclopropyl conjugation,[12] and steric inhibition of resonance,[11] yet the deviations were very similar.

In the case of **2**, Farnum and co-workers attributed the deviation to the relative twisting of the two aryl groups with respect to the plane of the trigonal cationic carbon as a result of increased electron demand upon the unsubstituted phenyl ring by the Z substituent. Thus, when

(1) For part 9 see: Brown, H. C.; Periasamy, M.; Perumal, P. T.; Kelly, D. P.; Giansiracusa, J. J. *J. Am. Chem. Soc.* **1983**, *105*, 6300–6305.
(2) Kelly, D. P.; Spear, R. J. *Aust. J. Chem.* **1977**, *30*, 1993–2004.
(3) Kelly, D. P.; Spear, R. J. *Aust. J. Chem.* **1978**, *31*, 1209–1221.
(4) Brown, H. C.; Kelly, D. P.; Periasamy, M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6956–6960.
(5) Brown, H. C.; Periasamy, M.; Liu, K.-T. *J. Org. Chem.* **1981**, *46*, 1646–1650.
(6) Kelly, D. P.; Jenkins, M. J.; Mantello, R. A. *J. Org. Chem.* **1981**, *46*, 1650–1653.
(7) Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1981**, *46*, 3161–3165.
(8) Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1981**, *46*, 3166–3170.
(9) Giansiracusa, J. J.; Jenkins, M. J.; Kelly, D. P. *Aust. J. Chem.* **1982**, *35*, 443–450.
(10) Brown, H. C.; Periasamy, M.; Kelly, D. P.; Giansiracusa, J. J. *J. Org. Chem.* **1982**, *47*, 2089–2101.
(11) Farnum, D. G.; Botto, R. E.; Chambers, W. T.; Lam, B. *J. Am. Chem. Soc.* **1978**, *100*, 3847–3855.
(12) Olah, G. A.; Berrier, A. L.; Arvanaghi, M.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 1122–1128.
(13) Olah, G. A.; Berrier, A. L.; Prakash, G. K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1998–2002.

0022-3263/84/1949-0409$01.50/0