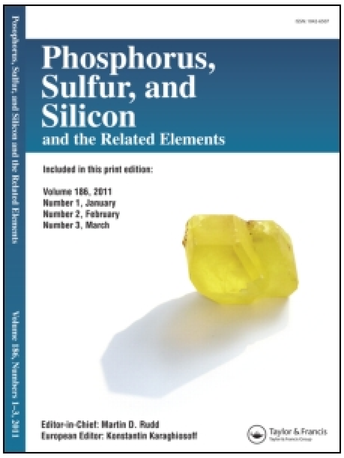


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ON THE ANIONS OF DIPHENYL 1-(4-NITROPHENYLAMINO)-1-ARYLMETHANE PHOSPHONATES[1]

Hans Zimmer[a]; M. W. Moore[a]; R. E. Koenigkramer[a]
[a] Department of Chemistry, University of Cincinnati, Cincinnati, Ohio

To cite this Article Zimmer, Hans , Moore, M. W. and Koenigkramer, R. E.(1988) 'ON THE ANIONS OF DIPHENYL 1-(4-NITROPHENYLAMINO)-1-ARYLMETHANE PHOSPHONATES1', Phosphorus, Sulfur, and Silicon and the Related Elements, 40: 3, 269 — 272

To link to this Article: DOI: 10.1080/03086648808072924

URL: http://dx.doi.org/10.1080/03086648808072924

Phosphorus and Sulfur, 1988, Vol. 40, pp. 269–272
Reprints available directly from the publisher
Photocopying permitted by license only

ON THE ANIONS OF DIPHENYL 1-(4-NITROPHENYLAMINO)-1-ARYLMETHANE PHOSPHONATES[1]

HANS ZIMMER,† M. W. MOORE,[2] and R. E. KOENIGKRAMER[3]
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

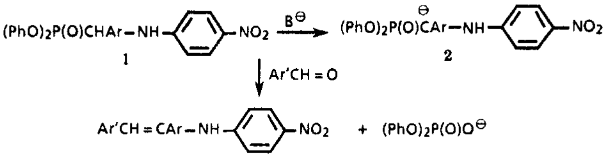
(Received July 8, 1988; in final form July 8, 1988)

By means of UV spectroscopy it is shown that the anions derived of diphenyl 1-(4-nitrophenylamino)-1-arylmethane phosphonates are carbanions and not nitranions. This spectroscopical finding is corroborated by alkylation of the anions to give almost quantitatively the C-alkylated products.

Key words: Diphenyl 1-(4-nitrophenylamino)-1-arylmethane phosphonates; diphenyl 1-(4-nitrophenylamino)-1-arylmethane phosphonate anion; UV spectra.

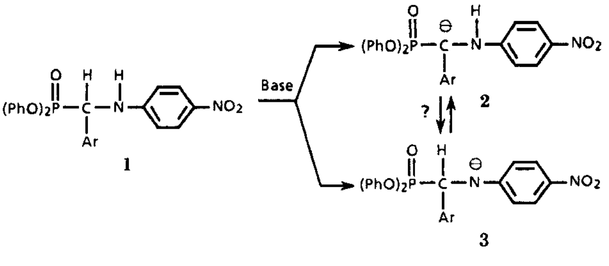
INTRODUCTION

In a series of papers we have demonstrated by the preparation of several classes of compounds the synthetic usefulness of diphenyl 1-(4-nitrophenylamino)-1-arylmethane phosphonates **1** as carbanion precursors **2**.[4a-1] The reaction of **2** with aromatic aldehydes yields enamines presumably in analogy to a Horner–Emmons reaction.



Ar = Ar' = various aromatic aldehydes

Because of the strong electron withdrawing nature of the nitro group in the 4 position of the phenylamino moiety, the question arose as to the exact position of the anion site. A phosphonate **1** upon deprotonation can conceivably lead either to the carbanion **2** or the nitranion **3**, or to an equilibrium between **2** and **3**.



It is obvious in order to obtain a Horner–Emmons product the anion **2** must react with the aldehyde. But this necessity does not exclude the possibility that **3**

---

† Author to whom all correspondence should be addressed.

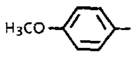
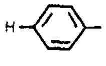
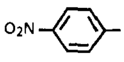
is actually the more thermodynamically stable anion because of the para nitro group's strong electron withdrawing ability with the concomitant resonance stabilization of the nitranion **3**. Thus, if an equilibrium exists between **2** and **3** and since the overall Horner-Emmons reaction is irreversible, **3** may indeed be the initially generated anion. The following study addresses this question through the use of UV spectroscopy and chemical transformations of the anionic species generated by deprotonation of **1**.

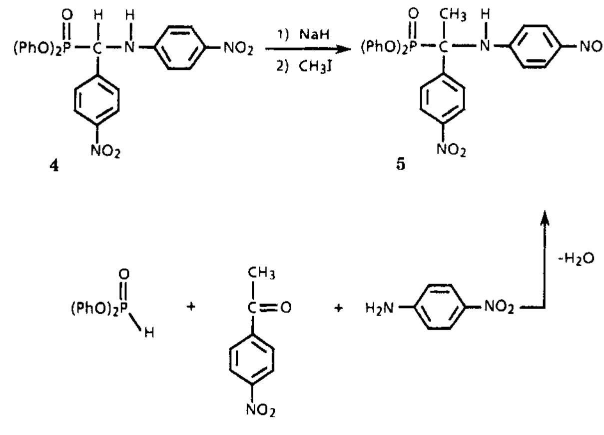
RESULTS AND DISCUSSION

Because the UV spectrum of 1 in methanol closely resembles a combination of the individual spectra of each chromophore (the substituted benzyl group and the 4-nitrophenylamino moiety respectively) a convenient method presented itself for the determination of the anionic site. Thus, the UV spectra of three phosphonates and their anions were taken between 200–400 mμ. The phosphonate spectrum of **1** consisted of essentially two absorptions due to the 4-nitrophenylamino moiety and to the benzyl moiety. Because of the electron delocalization of the anion into the aromatic ring, a bathochromic shift of the 4-nitrophenylamino moiety absorption implies structure **3**, whereas a bathochromic shift of the benzyl moiety implies structure **2**. As seen from Table I, in every case the absorption due to the ^1L_a band of the benzyl moiety is shifted to longer wavelengths—a bathochromatic shift—, whereas in none of the absorptions due to the ^1L_a band of the 4-nitrophenylamino group a shift to longer wavelengths occurred; the only shift which is observed due to this chromophore is a slight hypsochromic one. These observations clearly establish **2** as the more thermodynamically stable anion in this system. However, an equilibrium between **2** and **3** cannot unequivocally be ruled out because UV spectroscopy, as employed in this investigation, cannot detect **3** *if it is present only in amounts not exceeding about 5%*. This UV

Table I

UV Absorption of $(PhO)_2P(O)CH(Ar)$—NH——NO_2 and their Anions

Ar		λ max of 4-Nitrophenyl Amino moiety		λ max of 4-Substituted Benzyl moiety	
		λ	log ε	λ	log ε
H_3CO—	Neutral	367	.63	276	.2
	Anion	366	65	284	.08
H—	Neutral	366	1.75	260	.38
	Anion	366	1.65	292	.5
O_2N—	Neutral	362	1.53	262	1 12
	Anion	350	1.30	288	1.28



Scheme I

spectroscopical behavior of anions derived of **1** is also in agreement with ^{31}P and ^{13}C chemical shifts in the NMR spectra of these species as reported recently.[1]

In a further effort (Scheme I) to establish the anionic site also preparatively, the anion of diphenyl 1-(4-nitrophenyl)-1-(4-nitrophenylamino)methane phosphonate **4** was reacted with methyl iodide in dimethyl sulfoxide at 65°C to give the methylated product **5**. The structure of **5** was verified by an independent synthesis of **5** from diphenyl phosphite, 4-nitroacetophenone and 4-nitroaniline. As expected only C-alkylation was observed confirming a **2**-type structure as the more stable anion. These alkylation experiments however, again do not completely rule out the presence of small quantities of type **3** anions either, since if it is in facile equilibrium with type **2** it is only necessary that **2**-type anions alkylate faster than **3**-type ones for the mixture to appear to contain only the carbanion. It is interesting to note that attempted reactions of the anion of **5** with ethyl iodide, allyl bromide, benzyl bromide, acetyl chloride, carbon dioxide, carbon disulfide, or fluorenone under mild to rigorous conditions resulted only in starting materials being recovered. This suggests that though the phosphonate carbanion is formed, it however, is a rather poor nucleophile.

CONCLUSIONS

In summary, by the use of UV spectroscopy and chemical transformations it was determined that the anion derived of **1** predominantly is the carbanion **2**.

EXPERIMENTAL

The substituted diphenyl 1-(4-nitrophenylamino)-1-arylmethane phosphonates **1**, **2**, and **3** were prepared according to a one pot reaction as outlined earlier.[4g] The UV spectra were determined in absolute methanol on a Cary Model II recording spectrophotometer. The anions were generated by adding a small amount of KOH to the methanolic solutions of the phosphonate esters.

Diphenyl 1-(4-nitrophenylamino)-1-(4-nitrophenyl)-1-ethane phosphonate **5**: A solution of 1.5 g (2.97 mmol) of diphenyl 1-(4-nitrophenyl)-1-(4-nitrophenylamino)methane phosphonate in 2 ml of dimethylsulfoxide and 4 ml of THF was added to 0.14 g (3.04 mmol) of 50% NaH (which had been washed with dry hexane to remove the mineral oil). After adding 0.93 ml (15.0 mmol) of methyl iodide, the red solution was heated in a sealed flask at 70°C for 20 min. Upon dilution with 100 ml of chloroform, the solution was washed 3 times with 100 ml of water, 50 ml of 0.5 M $Na_2S_2O_3$, 50 ml of saturated NaCl solution, dried over anhyd. $MgSO_4$, and concentrated *in vacuo* to give the crude compound. It was recrystallized from 95% ethanol to give 1.09 g (70% yield) of pure product: m.p. 175.0–176.5°C; ^1H NMR ($CDCl_3$) δ 2.33 (d, 3H, $J = 18$ Hz), 5.83 (d, 1H, $J = 9$ Hz, D_2O exchangeable), 6.56 (d, 2H, $J = 9$ Hz) 6.9–7.5 (m, 10 H), 7.8–8.5 (m, 6 H): Anal. Calcd. for $C_{26}H_{22}N_3PO_7$: Calcd. C, 60.12; H, 4.27; N, 8.09; Found: C, 59.96; H, 4.20; N, 8.00.

ACKNOWLEDGEMENTS

The authors thank Lithium Corporation of America, Bessemer City, NC, (Dr. R. O. Bach) for generous gifts of *n*-butyllithium. R. E. Koenigkramer is grateful for financial assistance from the Material Science Grant established by Dr. George Rieveschl, Jr.

REFERENCES

1. This is part XVI of the series "Syntheses with α-Heterosubstituted Phosphonate Carbanions." Part XV: S. J. Smith, H. Zimmer, E. Fluck, and P. Fischer, *Phosphorus and Sulfur,* **35,** 105 (1988).
2. Ph.D. Thesis, University of Cincinnati, 1966.
3. Ph.D. Thesis, University of Cincinnati, 1980.
4. (a) H. Zimmer and P. J. Bercz, *Justus Liebigs Ann. Chem.,* **68,** 107 (1965); (b) H. Zimmer, P. J. Bercz, O. J. Maltenieks, and M. W. Moore, *J. Am. Chem. Soc.,* **87,** 2777 (1965); (c) H. Zimmer, P. J. Bercz, and G. E. Heuer, *Tetrahedron Lett.,* **171** (1968); (d) H. Zimmer and K. R. Hickey, *Angew. Chem.,* **83,** 942 (1971); (e) H. Zimmer, K. R. Hickey, and R. J. Schumacher, *Chimia,* **28,** 656 (1974); (f) H. Zimmer and D. M. Nene, *ibid,* **31,** 330 (1977); (g) P. D. Seemuth and H. Zimmer, *J. Org. Chem.,* **43,** 3063 (1978); (h) H. Zimmer and D. M. Nene, *J. Heterocycl. Chem.,* **15,** 1237 (1978); (i) R. E. Koenigkramer and H. Zimmer, *Tetrahedron Lett.,* 1017 (1980); (j) H. Zimmer, R. E. Koenigkramer, R. L. Cepulis, and D. M. Nene, *J. Org. Chem.,* **45,** 2018 (1980); (k) R. E. Koenigkramer and H. Zimmer, *ibid,* **45,** 3394 (1980); (l) D. W. Burkhouse and H. Zimmer, *Synthesis,* 330 (1984).