H. R. Barton for his comments upon the manuscript, and Drs. Goutarel and P. Potier for their encouragement.

Registry No.—**1,** 7785-26-4; **2,** 68036-78-2; **2** HCl, 68036-79-3; **3,** 68036-80-6; **3a,** 68036-81-7; **3b,** 68036-82-8; **3c,** 68036-83-9; **3c** N–Ac derivative, 68036-84-0; **3c** HCl, 68070-06-4; **4,** 68036-85-1.

References and Notes

(1) Taken in part from the "Thèse de Doctorat es-Sciences" of B. Delpech, Université de Paris-Sud, Centre d'Orsay, 1977.
(2) H. C. Brown and J. T. Kurek, *J. Am. Chem. Soc.*, **91,** 5647 (1969).
(3) B. Delpech and Q. Khuong-Huu, *Tetrahedron Lett.*, 1533 (1973).
(4) Z. Rappoport, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, **94,** 2320 (1972).
(5) A. I. Meyers and J. J. Ritter, *J. Org. Chem.*, **23,** 1918 (1958); J. Schneller and N. K. Ralhan, *ibid.*, **28,** 2944 (1963).
(6) C. A. Grob and P. W. Schiess, *Angew. Chem., Int. Ed. Engl.*, **6,** 1 (1967); C. A. Grob, *ibid.*, **8,** 535 (1969).
(7) W. N. Speckamp, J. Dijkink, and H. O. Huisman, *Chem. Commun.*, 196, 197 (1970); A. W. J. D. Dekkers, W. N. Speckamp, and H. O. Huisman, *Tetrahedron Lett.*, 489 (1971); W. N. Speckamp, J. Dijkink, A. W. J. D. Dekkers, and H. O. Huisman, *Tetrahedron*, **27,** 3143 (1971).
(8) H. Stetter and W. Reinartz, *Chem. Ber.*, **105,** 2773 (1972).
(9) R. C. Fort, Jr., in "Adamantane, The Chemistry of Diamond Molecules", P. G. Gassman, Ed., Marcel Dekker, New York, 1976, p 268.

(2,3,3′,4,4′,5,5′-Heptacyanocyclopent-1-enyl)triphenylphosphazene. Structural Revision of a Percyanophospholidine

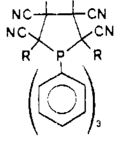
H. Fritz and C. D. Weis*

Central Research and Dyestuffs and Chemicals Department, Ciba-Geigy Corp., Basle, Switzerland

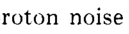
Received July 13, 1978

The reaction of 2 mol of tetracyanoethylene with 1 mol of triphenylphosphine was reported in 1963, and the structure (**1a**) of the adduct formed was assumed to be that of an octacyano-*P,P,P*-triphenylphospholidine.[1] The chemical evidence for this reasoning rested upon the analytical results and the acidic degradation of the adduct, which yielded butane tetracarboxylic acid and triphenylphosphine oxide. Further support came from the interpretation of the ^{31}P NMR spectrum, and in particular the comparison of the phosphorus chemical shift with those of organic phosphorus compounds of known structures. A compound possessing the triphenylphosphazene structure (**2**) with a four-coordinate quinquevalent phosphorus also might have been formed, and was originally proffered as an alternative, but rejected on the above grounds, and also as it would necessitate an improbable migration of a triphenylphosphine unit from a carbon to a nitrogen atom on the other end of the percyanocarbon chain.

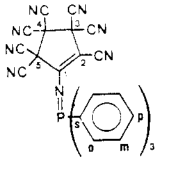
This paper corrects the originally assumed structure **1a** and offers ^{13}C NMR spectroscopic evidence for structure **2.** Also from ^{13}C spectroscopic data structure **3** is deduced for the product of methanol addition for which originally the bisimino ether of structure **1b** was proposed.[1]



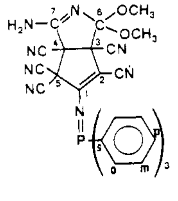
1a, R = CN



1b, $R = C\genfrac{}{}{0pt}{}{\nearrow NH}{\searrow OCH_3}$



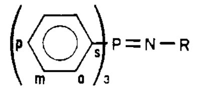
2

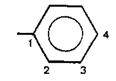
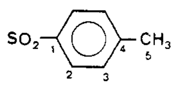


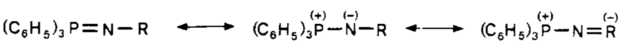
3

Structure **1a** can immediately be excluded because of the number of chemically shifted carbon signals observed in the proton noise decoupled ^{13}C NMR spectrum of the TCNE adduct. In order to distinguish between chemical shifts and ^{13}C, ^{31}P coupling constants, spectra were taken at frequencies of 25.2 and 90.5 MHZ.

The ^{13}C spectra of compounds **4–7** with known structure[2] were recorded for comparison, so as to verify the phosphinimine structures **2** and **3.** Further ^{13}C data for phosphazenes appeared recently in the literature.[3]



Compound	R
4	$\underset{1}{C}H_3$
5	
6	$\underset{1}{COO}-\underset{2}{C}(\underset{3}{CH_3})_3$
7	



$$(C_6H_5)_3P{=}N{-}R \longleftrightarrow (C_6H_5)_3\overset{(+)}{P}{-}\overset{(-)}{N}{-}R \longleftrightarrow (C_6H_5)_3\overset{(+)}{P}{-}N{=}\overset{(-)}{R}$$

a b c

Values of ^{13}C chemical shifts and ^{13}C, ^{31}P coupling constants are given in Table I.

Table I. ^{13}C Chemical Shifts[a] and ^{13}C, ^{31}P Coupling Constants[b] of Phosphazenes 2–7

C atom	**4**[f]	**5**[g]	**6**[h]	**7**[i]	**2**[j]	**3**[k]
s	131.1 (95.1)	131.1 (98.8)	128.8 (101.1)	127.3 (104.2)	124.4 (103.8)	126.2 (103.2)
0	132.5 (8.7)	132.5 (9.4)	133.1 (9.8)	133.1 (10.8)	132.7 (11.1)	132.1 (10.8)
m	128.4 (11.4)	128.5 (11.5)	128.5 (12.3)	128.7 (13.0)	130.2 (13.2)	129.6 (12.9)
p	131.3 (2.7)	131.5 (2.4)	132.1 (2.8)	132.8 (3.0)	134.6 (3.0)	133.8 (3.0)
1	31.7 (6.4)	151.1 (2.5)	161.2 (1.0)	143.6 (2.9)	154.6 (1.1)	156.7 (1.0)
2		123.4 (17.5)	77.7 (2.4)	125.7	73.8 (5.4)	76.2 (5.7)
3		128.5 (1.3)	28.3	128.6	47.3[c]	59.7[c]
4		117.3 (0.6)		140.4	47.4[c] (1.1)	62.2[c] (1.0)
5				21.2	52.6 (23.1)	49.8 (23.4)
6						118.2
7						158.8
other					*d*	*e*

[a] δ values in ppm (±0.1 ppm) at 25.156 MHz, internal standard Me_4Si ($\delta = 0$), solvent $CDCl_3$ for **2** and **4–7,** Me_2SO-d_6 for **3,** concentration about 0.3 M. [b] In Hz (±0.2 Hz), given in parentheses below δ values. Where no value is given, the coupling constant is smaller than 0.3 Hz. [c] Assignments may be reversed. [d] CN carbon signals at 112.2, 107.8, 107.6 (1.5), and 106.4 (0.7) ppm. [e] CN carbon signals at 114.5, 113.4, 113.3 (1.5), 111.9 (1.5), and 110.5 (1.1) ppm. OCH_3 carbon signals at 53.1 and 51.3 ppm. [f] Registry no. 17986-01-5. [g] Registry no. 2325-27-1. [h] Registry no. 68014-21-1. [i] Registry no. 1058-14-6. [j] Registry no. 68014-22-2. [k] Registry no. 68014-23-3.

0022-3263/78/1943-4900$01.00/0

Assignment of the signals of the triphenylphosphine carbons is straightforward for all products, and is in accord with assignments given for similar compounds.[3-5]

For compounds **4-7**, assignment of the carbon signals of the substituent R can also directly be made from chemical shifts, C, P coupling constants, and relative intensities. Our data are in complete agreement with those presented earlier.[2]

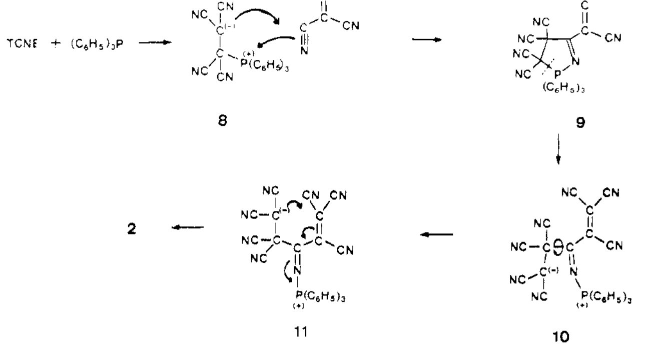
Although not all of the signals of the phosphazene substituent in **2** and **3** can be assigned to individual carbon atoms, the number of signals, their multiplicities, and intensities are fully consistent with the proposed structures. Thus, for compound **2** four signals for CN carbons with an intensity ratio of 1:2:2:2 are observed at 112.2 (CN at C-2), 107.8, 107.6, and 106.4 ppm (the intensities were measured at low pulse angles to avoid saturation).[6] For compound **3**, the CN carbons give rise to five signals of approximately equal intensity between 114.5 and 110.5 ppm. The sp^2 hybridized carbons C-1 and C-2 can directly be identified from their characteristic chemical shifts and C, P coupling constants. The chemical shifts indicate the presence of a strongly polarized double bond. The last of the three sp^3 carbon atoms C-3, C-4, and C-5 can be distinguished from the other two because of its large three-bond C, P coupling constant.

In compound **3**, the carbon signal at 118.2 ppm displays septet structure in the proton undecoupled spectrum, indicating coupling with the protons of two methyl groups (J = 4.2 Hz) as is expected for carbon C-6. That the signal at 158.8 ppm corresponds to a carbon atom with an attached NH$_2$ group is shown by the typical deuterium isotope effect on the chemical shift of this signal;[7] after addition of a 1:1 mixture of H$_2$O/D$_2$O to a Me$_2$SO-d_6 solution of **3**, the signal at 158.8 ppm appears as a triplet with an intensity ratio of 1:2:1 and a splitting of 2.0 Hz (at 25.2 MHZ) in the proton noise decoupled ^{13}C spectrum. The three signals correspond to carbons having a NH$_2$, NHD, and ND$_2$ group attached, displaying an isotope effect of 0.08 ppm/D atom, typical of a two-bond effect.[7]

As has been shown for triphenylphosphoranes,[4] bonding in triphenylphosphazenes can be discussed in terms of valence bond structures **a** to **c**, where the phosphonium saltlike structure **c** is only important for compounds in which the substituent R can stabilize the negative charge by resonance. The ^{13}C spectroscopic parameters in such compounds are expected to be similar to the ones observed in phosphonium salts (chemical shifts and C, P coupling constants or phosphonium salts are reported in the literature[3-5,8]).

From the parameters observed for **2** and **3** (especially chemical shifts of C-s and C-p) and ^1J (C-s, P), it can be concluded that valence bond structure **c** is important for the description of bonding in these compounds. The zwitterionic character in **2** and **3** is also evident from the large chemical shift difference between C-1 and C-2.

Recent investigations point to a completely different explanation for the formation of **2** to that presented earlier.[1]



Tetracyanoethylene and triphenylphosphine form rapidly a 1,3-dipolar intermediate (**8**) which subsequently reacts in a [3 + 2] cycloaddition with one of the cyano groups of TCNE forming a five-membered azaphospholene intermediate of structure **9**.

The adduct **8** is a new type of highly reactive 1,3-dipolar intermediate[9,10] with phosphorus as one of the terminal centers of a zwitterionic species which represents a reactive type without double bond. Cycloadditions of 1,3-dipolar species on nitrile groups have been reported by several authors[11-13] although the rate of reaction in general appears to be very slow. Reversible cleavage of the P-C bond in **9** gives rise to **10**, whereby further stabilization is enhanced by the dicyano methide group despite the large separation of the ionic centers.[14-16] Rotation about the C-C bond as indicated (**10** → **11**) and subsequent cyclization of the zwitterion leads to the formation of a new C-C bond between C-3 and C-4 yielding **2**.

Experimental Section

Compounds **2-7** were prepared by literature procedures.[1,2] The ^{13}C-NMR spectra were recorded on Varian XL-100/15 (25.2 MHz) and Bruker HX-360 (90.5 MHz) NMR spectrometers in the Fourier mode with either proton noise decoupling, coherent off-resonance decoupling, or gated noise decoupling (for undecoupled spectra or NOE suppression). The numbers of data points and sweep widths were chosen such that an accuracy of 0.05 ppm for chemical shifts and 0.2 Hz for C, P coupling constants was achieved.

Registry No.—**1a**, 17989-88-7; **1b**, 68014-24-4.

References and Notes

(1) G. S. Reddy and C. D. Weis, *J. Org. Chem.*, **28**, 1822 (1963).
(2) W. Wiegräbe and H. Bock, *Chem. Ber.*, **101**, 1414 (1968).
(3) T. A. Albright, W. J. Freeman, and E. E. Schweizer, *J. Am. Chem. Soc.*, **97**, 940 (1975); (b) T. A. Albright, W. J. Freeman, and E. E. Schweizer, *J. Org. Chem.*, **41**, 2716 (1976).
(4) G. A. Gray, *J. Am. Chem. Soc.*, **95**, 7736 (1973).
(5) T. A. Albright, W. J. Freeman, and E. E. Schweizer, *J. Org. Chem.*, **40**, 3437 (1975).
(6) J. N. Shoolery, "Progress in NMR Spectroscopy", Vol. 11, J. M. Emsley, J. Feeney, and L. H. Sutcliffe, Eds., Pergamon Press, New York, N.Y., 1977, p 79.
(7) J. Feeney, P. Partington, and G. C. K. Roberts, *J. Magn. Reson.*, **13**, 268 (1974).
(8) (a) T. A. Albright, W. J. Freeman, and E. E. Schweizer, *J. Am. Chem. Soc.* **97**, 2942 (1975); (b) T. A. Albright, W. J. Freemen, and E. E. Schweizer, *ibid.*, **97**, 2946 (1975).
(9) R. Huisgen, *Angew. Chem.*, **75**, 604 (1963).
(10) R. Huisgen, *J. Org. Chem.*, **41**, 403 (1976).
(11) R. M. Scribner, G. N. Sausen, and W. W. Pritchard, *J. Org. Chem.*, **25**, 1440 (1960).
(12) K. Burger, H. Schickaneder, and M. Pinzel, *Justus Liebigs Ann. Chem.*, 30 (1976).
(13) A summary of prior work is given by K. Burger and J. Fehn, *Chem. Ber.*, **105**, 3814 (1972).
(14) D. Kaufmann, A. de Mejere, B. Hingerty, and W. Saenger, *Angew. Chem.*, **87**, 842 (1975).
(15) A. Efraty, *Chem. Rev.*, **77**, 691 (1977).
(16) M. Nakahara, Y. Tsuda, M. Sasaki, and J. Osugi, *Chem. Lett.*, 731 (1976).

Nucleophilicity of Cycloheptatrienyldiene Generated from a Nitrogen-Free Precursor. Evidence for a Free Carbene in the Decomposition of Tropone Tosylhydrazone Sodium Salt

B. L. Duell[1] and W. M. Jones*

Department of Chemistry, University of Florida, Gainesville, Florida 32611

Received May 22, 1978

In a previous study of the reactivity of the aromatic carbene cycloheptatrienylidene (**1**) [and/or cycloheptatetraene (**5**)] with substituted styrenes in THF solution, a ρ value of +1.05 ± 0.05 (correlation coefficient 0.982) was determined.[2] From this it was argued that the reacting species has considerable

0022-3263/78/1943-4901$01.00/0