was dried over anhydrous Na_2SO_4, and the solvents were removed under vacuum. $CHCl_3$ was added to the residue and the insoluble part (**2**) separated. The soluble part was filtered through a column of silica, and the products (**5**, **6**, **7**, and **8**) were isolated from among the tarry materials.

5: mp 159–160 °C (yellow crystals from acetone); IR (KBr) 3330, 1630 cm^{-1}; NMR (CCl_4) δ 1.0–2.0 (m, 30 H), 2.80 (m, 3 H), 6.97 (s, 1 H); mass spectrum, *m/e* 370.5 (M^+). Anal. Calcd for $C_{24}H_{34}O_3$: C, 77.80; H, 9.25. Found: C, 77.67; H, 9.30.

6: mp 77–79.5 °C (orange crystals from petroleum ether); IR (KBr) 3370, 1640 cm^{-1}; NMR (CCl_4) δ 1.0–2.0 (m, 20 H), 2.80 (m, 2 H), 6.28 (s, 1 H), 6.80 (s, 1 H); mass spectrum, *m/e* 288 (M^+). Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.72; H, 8.17.

7: mp 205–208.5 °C (orange crystals from acetone); IR (KBr) 3340, 1610 cm^{-1}; NMR ($CDCl_3$) δ 1.1–2.0 (m, 20 H), 2.80 (m, 2 H), 7.86 (s, 2 H); mass spectrum, *m/e* 304 (M^+). Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.02; H, 7.95. Found: C, 68.83; H, 7.68.

8: mp 134.5–137.5 °C subl. (orange plates from CCl_4); IR (KBr) 3320, 1615 cm^{-1}; NMR (CCl_4) δ 1.0–2.0 (m, 10 H), 2.80 (m, 1 H), 5.91 (s, 1 H), 7.76 (s, 2 H); mass spectrum, *m/e* 222 (M^+). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.54; H, 6.56.

The reactions of the boranes with excess amounts of **2** were carried out similarly; isolation was performed on a 5-mmol scale (borane), and excess **2** was recovered substantially. ^1H NMR analysis was performed on a 1-mmol scale (Table I). Dimethyl oxalate was used as an internal standard, and the yields were determined by the area ratio of its CH_3 signal to the olefinic signals of **6** and **8**. Although the yields of **5** and **7** could not be determined by this method, TLC analysis revealed that only small amounts of these quinones were formed.

Reaction of 2 with 14. To a DMF solution of **2** (0.84 g, 6 mmol) was added **14** (0.48 mL, 2 mmol) at 0 °C as described above. A similar isolation procedure using a column of silica gave **15** and **16**. **15**: mp 38–39 °C (yellow needles); IR (KBr) 3320, 1635 cm^{-1}; NMR ($CDCl_3$) δ 0.66–1.90 (m, 21 H), 2.10–2.70 (m, 6 H), 6.87 (s, 1 H); mass spectrum, *m/e* 292 (M^+). Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.97; H, 9.59. Found: C, 73.69; H, 9.68. **16**: mp 150–155 °C (sealed tube) (orange plates from $CHCl_3$); IR (KBr) 3320, 1620 cm^{-1}; NMR ($CDCl_3$) δ 0.80–1.14 (m, 6 H), 1.14–1.70 (m, 8 H), 2.34–2.60 (m 4 H), 7.58 (s, 2 H); mass spectrum, *m/e* 252 (M^+). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.58; H, 8.10.

Reaction of 17 with Organoboranes. A THF solution of **4** (2 mmol) was added to a DMF (10 mL) solution of **17** (336 mg, 1.5 mmol) at 0 °C under N_2. The resulting mixture was stirred overnight and then heated at 50 °C for 30 min. A similar isolation method using a column of silica gave **5** (<1%), **19** (15 mg, 2%), and **18** (166 mg) contaminated with small amounts of 2,5-diacetoxyhydroquinone. Oxidation of **18** by the reported procedure[13] with $NaClO_3$ (0.03 g,), V_2O_5 (0.3 mg), and a 2% H_2SO_4 solution (0.54 mL) afforded **20** (39 mg) along with small amounts of **17** (<6 mg). Aqueous NaOH solution (2 N) was added to an acetone solution of **20**, and the resulting mixture was stirred for 2 h. The color changed from red-purple to yellow when the mixture was acidified with HCl. Extraction with ether gave **8** quantitatively. **19**: mp 182–192 °C subl. (light yellow crystals); IR (KBr) 1775, 1665, 1625 cm^{-1}; NMR (CCl_4) δ 1.0–2.1 (m, 20 H), 2.32 (s, 6 H), 2.75 (m, 2 H); mass spectrum, *m/e* 346, 304.

Hydrolysis of **19** gave **7**. **20**: mp 72–75 ° C (light yellow crystals from hexane); IR (KBr) 1780, 1675, 1620 cm^{-1}; NMR (CCl_4) δ 1.1–2.0 (m, 10 H), 2.31 (s, 3 H), 2.33 (s, 3 H), 2.76 (m 1 H), 6.44 (s, 1 H); mass spectrum, *m/e* 264, 222.

The reaction of **17** (1.6 mmol) with **14** (1.6 mmol) was carried out similarly. The isolation procedure was as follows. The insoluble part in $CHCl_3$ (**22**) was oxidized by the reported procedure[13] to give 2,5-diacetoxy-3,6-di-*n*-butyl-1,4-benzoquinone (30 mg, 6%): mp 115–118 °C (yellow crystals); IR (KBr) 1780, 1675, 1625 cm^{-1}; NMR ($CDCl_3$) δ 0.76–1.08 (m, 6 H), 1.08–1.60 (m, 8 H), 2.20–2.68 (m, 10 H), involving 2.33 (s, 6 H); mass spectrum, *m/e* 294, 252. Hydrolysis of this quinone gave **16**. The soluble part in $CHCl_3$ was filtered through a column of silica to afford **21** (106 mg, 25%): mp 104–108 °C (yellowish white crystals); IR (KBr) 3365, 1740, 1604 cm^{-1}; NMR ($CDCl_3$) δ 0.76–1.10 (m, 3 H), 1.10–1.64 (m, 4 H), 2.24–2.52 (m, 8 H) involving 2.34 (s, 6 H), 5.63 (s, 1 H), 6.59 (s, 2 H); mass spectrum, *m/e* 282 (M^+). Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.56; H, 6.43. Found: C, 59.42; H, 6.49.

Synthesis of Rapanone (26). A THF solution of **17** (448 mg, 2 mmol) was added to a THF solution of **23** (2 mmol) at 0 °C. The color of the solution was still red-purple after 24 h and almost faded away by refluxing for 3 h. Extraction and a drying process were carried out as described above. Separation of the insoluble part of the residue in CCl_4 gave crude **24** (white precipitate, 384 mg). Oxidation of **24** (204 mg) by the standard procedure[13] ($NaClO_3$, 30 mg; V_2O_5, 0.3 mg; 2% H_2SO_4 solution, 0.5 mL), followed by filtration through a column of silica, gave **25** (62 mg) along with **17** (25 mg). Hydrolysis of **25** by the same procdure as described above gave **26** quantitatively. The total yield from **17** was 17%.

25: mp 52–54.5 °C (yellow crystals); IR (KBr) 1770, 1675, 1625 cm^{-1}; NMR ($CDCl_3$) δ 0.70–1.70 (m, 25 H), 2.27–2.52 (m, 8 H), involving 2.36 (s, 6 H), 6.62 (s, 1 H); mass spectrum, *m/e* 322.

26: mp 137–142 °C (lustrous orange plates from CCl_4) (lit. mp 139–142[14] and 141–142 °C[15]); IR (KBr) 3320, 1615 cm^{-1}; NMR ($CDCl_3$) δ 0.80–1.66 (m, 25 H), 2.48 (m, 2 H), 6.03 (s, 1 H), 7.70 (s, 2 H).

Acknowledgment. Financial support from the Ministry of Education, Science and Culture (Grant 247020) and from JSPS (Basic Chemical Research Foundation) is gratefully acknowledged.

Registry No.—**2**, 615-94-1; **3**, 32999-09-0; **4**, 1088-01-3; **5**, 68014-08-4; **6**, 68014-09-5; **7**, 68014-10-8; **8**, 68014-11-9; **14**, 122-56-5; **15**, 68014-12-0; **16**, 68014-13-1; **17**, 16523-32-3; **18**, 68014-14-2; **19**, 68014-15-3; **20**, 68014-16-4; **21**, 68014-17-5; **22**, 68014-18-6; **23**, 68014-19-7; **24**, 68014-20-0; **25**, 2552-83-2; **26**, 573-40-0.

References and Notes

(1) R. H. Thomson, "Naturally Occurring Quinones", 2nd ed., Academic Press, New York, 1971.
(2) M. F. Hawthorne and M. Reintjes, *J. Am. Chem. Soc.*, **86**, 951 (1964); **87**, 4585 (1965).
(3) G. W. Kabalka, *J. Organomet. Chem.*, **33**, C25 (1971).
(4) B. M. Mikhailov, G. S. T.-Sarkisyan, and N. A. Nikolaeva, *Zh. Obshch. Khim.*, **41**, 1721 (1971); *Chem. Abstr.*, **76**, 3934n (1972).
(5) H. W. Moore and R. J. Wikholm, *Chem. Quinoid Compd. 1974*, **1**, 425 (1974).
(6) H. C. Brown and M. M. Midland, *Angew. Chem., Int. Ed. Engl.*, **11**, 692 (1972).
(7) B. M. Mikhailov, G. S. T.-Sarkisyan, and N. A. Nikolaeva, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 527 (1968).
(8) H.-D. Becker, *Chem. Quinoid Compd. 1974*, **1**, 335 (1974).
(9) "Dictionary of Organic Compounds", Vol. 2, Maruzen, Tokyo, 1965, p 1058: $pK_1 = 5.18$, $pK_2 = 2.73$.
(10) There is a possibility that **10** instead of **11** reacts further with R_3B.
(11) K. T. Finley, *Chem. Quinoid Compd. 1974*, **2**, 877 (1974).
(12) H. C. Brown and E. Negishi, *J. Am. Chem. Soc.*, **93**, 3777 (1971).
(13) H. W. Underwood, Jr., and W. L. Walsh, "Organic Syntheses", Collect. Vol. 2, Wiley, New York, 1943, p 553.
(14) M. Asano and K. Yamaguchi, *Yakugaku Zasshi*, **60**, 585 (1940).
(15) L. F. Fieser and E. M. Chamberlin, *J. Am. Chem. Soc.*, **70**, 71 (1948).
(16) H. C. Brown, "Organic Synthesis via Boranes", Wiley-Interscience, New York, 1975.
(17) R. G. Jones and H. A. Shonle, *J. Am. Chem. Soc.*, **67**, 1034 (1945).
(18) A. H. Crosby and R. E. Lutz, *J. Am. Chem. Soc.*, **78**, 1233 (1956).

Convenient Two-Step Synthesis of Substituted 1-Azaadamantanes from α-Pinene[1]

B. Delpech and Q. Khuong-Huu*

Institut de Chimie des Substances Naturelles, Centre National de la Recherche Scientifique, 91190-Gif/Yvette, France

Received July 18, 1978

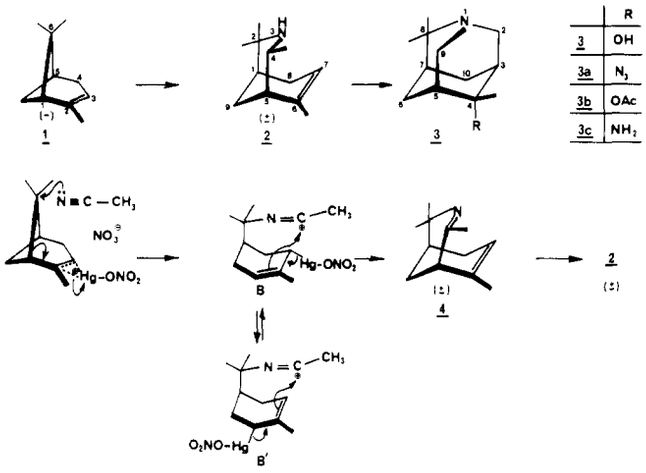
The solvomercuration–demercuration of olefins in the presence of acetonitrile provides a convenient technique for the Markownikoff amidation of carbon–carbon double bonds[2] or for allylic amidation.[3] Nevertheless, the treatment of α-pinene (**1**) with acetonitrile in the presence of mercuric nitrate followed by in situ borohydride reduction did not afford the expected amide, but led instead to azabicyclo[3.3.1]nonene **2** (Scheme I).

In imino olefinic structure **2**, the relative positions of the nitrogen atom and of the double bond permitted a one-step synthesis, via an iminium intermediate, of 1-azaadamantane of type **3** in virtually quantitative yield.

The 2,2,4,6-tetramethyl-3-azabicyclo[3.3.1]non-6-ene (**2**) was obtained in 51% yield as the hydrochloride. The racemic intermediate **4** was isolated when the reaction was carried out without borohydride reduction. Racemization of the imine **4**

0022-3263/78/1943-4898$01.00/0

Scheme I



apparently arises from the rapid equilibrium of the allylic organomercurials B and B'.[4] The formation of the azabicyclononene **4** resulted from an intramolecular cyclization via azocarbenium B and B'. An analogous cyclization has been observed when the Ritter reaction was carried out on a hydroxy olefin.[5]

Olefin **2**, with formaldehyde and acid catalysis, afforded 1-azaadamantanol **3** in 88% yield. In this step, one observes the loss of the C-9 methyl. The mechanism in Scheme II is proposed to explain this phenomenon.

Cyclization of the iminium intermediate **2a** led to the 1-azaadamantanol **2b**. The strong steric interaction between the 1,3-diaxial C-4, C-9 methyl groups and the geometrical relationship between the nitrogen lone pair orbital and the leaving group induced a Grob-type fragmentation,[6] giving the iminium olefin **2c**. In situ hydrolysis of **2c** with loss of acetaldehyde led to the olefinic amine **2d**. The excess of formaldehyde provided the iminium salt **2e**, which afforded finally the 1-azaadamantanol **3**. The proposed mechanism (Scheme II) is in good agreement with the obtention of the tetradeuteriated 1-azaadamantanol **3d** when the reaction was carried out on deuteriated formaldehyde ($D_2C{=}O$). Compound **2** is a versatile intermediate for the synthesis of 1-azaadamantane compounds substituted at C-4. Thus, by an appropriate choice of nucleophile, N_3^- or OAc^-, the cyclization of **2** via an iminium intermediate can afford the corresponding azide **3a** or acetoxyl **3b** (Scheme I). Olefin **2**, treated with formaldehyde and sodium azide, gave the azide **3a**. The latter is easily reduced by $LiAlH_4$ to the amine **3c**.

The previously reported synthesis of 1-azaadamantane derivatives[7,8] involved long multistep sequences.[9]

The ready accessibility of α-pinene renders our synthesis both convenient and inexpensive. It opens the way to the synthesis of various other azaadamantanes.

Experimental Section

Melting points were determined with a Büchi apparatus. IR spectra were obtained on a Perkin-Elmer Model 257 spectrometer in Nujol mulls, the NMR spectra were recorded with a Varian A-60 and a Brucker HX 90E spectrometer. Mass spectra were determined on an AEI MS9 instrument. Microanalyses were performed by the Service Central de Microanalyse du C.N.R.S.

2,2,4,6-Tetramethyl-3-azabicyclo[3.3.1]non-6-ene (2). A mixture of anhydrous mercuric nitrate (2.5 g, 7.7 mmol) in acetonitrile (50 mL) in the presence of molecular sieves was stirred at 0 °C, and α-pinene (1 g, 7.3 mmol) was added. The mixture was stirred overnight at ambient temperature and cooled at 0 °C; 3 N sodium hydroxide (10 mL) and 0.5 N sodium borohydride in 3 N sodium hydroxide (10 mL) were added. After 1 h, the filtrate was extracted with ether (4 × 40 mL). The ethereal phase was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was dissolved in pentane (the insoluble part was eliminated) and treated with ethereal hydrogen chloride. Recrystallization of the precipitate from acetone afforded 0.80 g of the hydrochloride of **2** (51%), mp >260 °C. Anal. Calcd for $C_{12}H_{21}N{\cdot}HCl$: C, 66.80; H, 10.28; N, 6.49. Found: C, 66.67; H, 10.34; N, 6.54. The corresponding base **2** is a noncrystallizable oil: IR (film) 3380 cm^{-1}; ^1H NMR δ 0.96 (d, 3 H, J = 7 Hz, Me C-4), 1.06, 1.19 (s, 6 H, 2Me C-2), 1.69 (m, 3 H, Me C-6), 3.11 (q, 1 H, J = 7 Hz, J' = 2 Hz, H-4), 5.52 (m, 1 H, H-7); ^{13}C NMR δ 34.4 (C-1), 53.3 (C-2), 49.9 (C-4), 39.9 (C-5), 133.4 (C-6), 124.1 (C-7), 29.0 (C-8), 27.6 (C-9), 25.8, 30.0 (2Me C-2), 21.9 (Me C-4), 25.5 (Me C-6).

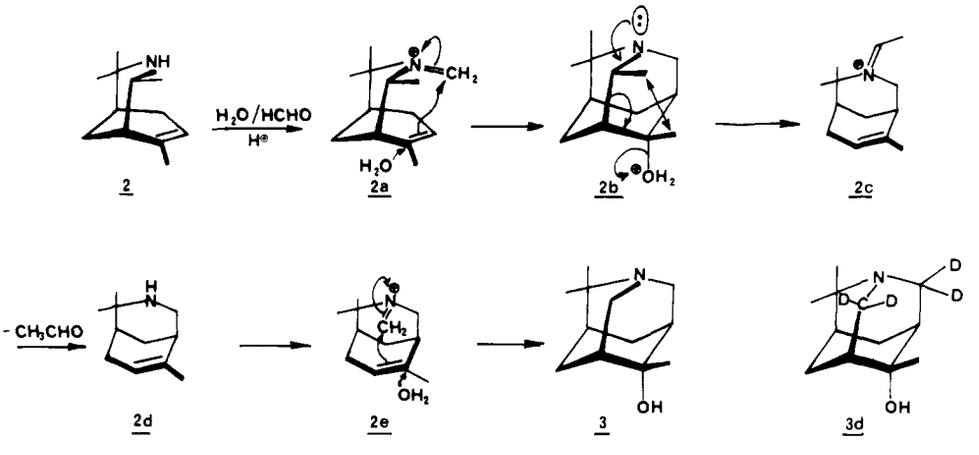
4,8,8-Trimethyl-4-hydroxy-1-azaadamantane (3). A solution of the hydrochloride of **2** (1.5 g, 7 mmol) in dioxane (36 mL) and 40% aqueous formaldehyde (4 mL) was treated in a steam bath for 1.5 h. The solution was basified by NaOH and extracted by methylene chloride. The crude base **3** was recrystallized from acetone (1.19 g, 88%): mp 177–178 °C; IR 3130 cm^{-1}; ^1H NMR δ 1.25 (s, 2Me C-8), 1.34 (s, Me C-4), 3.2 (AB, J_{AB} = 14 Hz, $2CH_2$ C-2 and C-9); ^{13}C NMR δ 50.6 (C-2, C-9), 38.0 (C-3, C-5), 71.7 (C-4), 27.0 (C-6, C-10), 34.1 (C-7), 56.0 (C-8), 25.9 (Me C-4), 26.3 (Me C-8). Anal. Calcd for $C_{12}H_{21}NO$: C, 73.79; H, 10.84; N, 7.17. Found: C, 73.62; H, 10.89; N, 7.28.

4,8,8-Trimethyl-4-azido-1-azaadamantane (3a). Azide **3a** was prepared by the above procedure, with the addition of sodium azide in the reaction mixture (1.5 g, 23 mmol, 85%): mp 60 °C (acetone); IR 2110 cm^{-1}; ^1H NMR δ 1.25 (s, 2Me C-8), 1.49 (s, Me C-4), 3.18 (A_2B_2, J_{AB} = 14 Hz, $2CH_2$ C-2, C-9); ^{13}C NMR δ 49.7 (C-2, C-9), 34.8 (C-3, C-5), 66.2 (C-4), 27.6 (C-6, C-10), 32.8 (C-7), 55.3 (C-8), 21.7 (Me C-4), 26.5 (Me C-8); mass spectrum, m/e 220 (M^+). M − 28, M − 42.

4,8,8-Trimethyl-4-amino-1-azaadamantane (3c). A mixture of azide **3a** (270 mg, 1.2 mmol) in ether (40 mL) and $LiAlH_4$ (150 mg, 4 mmol) was heated to reflux for 6 h. Extraction with ether afforded 220 mg of the amine **3c** (92%): IR 3300, 1650, 1535 cm^{-1}. N-Ac derivative: mp 115 °C (acetone); IR 1625, 1570 cm^{-1}; ^1H NMR δ 1.30 (s, 2Me C-8), 150 (s, Me C-4), 1.95 (s, $COCH_3$). HCl derivative, mp >260 °C (MeOH).

Acknowledgment. We thank the Ligue Nationale Française contre le Cancer for a grant to B. Delpech, Professor D.

Scheme II



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

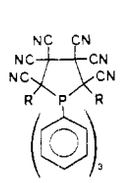
H. Fritz and C. D. Weis*

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

Received July 13, 1978

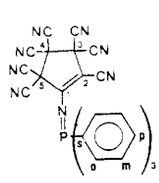
The reaction of 2 mol of tetracyanoethylene with 1 mol of triphenylphosphine was reported in 1963, and the structure (**1a**) of the adduct formed was assumed to be that of an octacyano-*P,P,P*-triphenylphospholidine.[1] The chemical evidence for this reasoning rested upon the analytical results and 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]

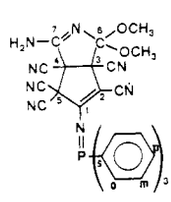


1a, R = CN

1b, R = C(=NH)OCH$_3$



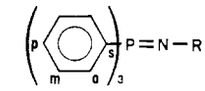
2

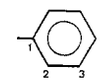
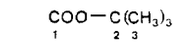
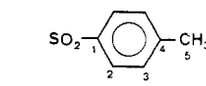


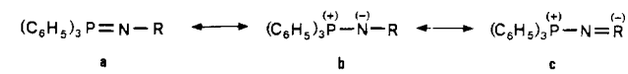
3

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	
5	
6	
7	



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 (δ = 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