COMMUNICATIONS

by reaction of the elements and condensed fractionally, SbF$_5$ was fractionally distilled, and HF and DF were dried with fluorine.[13]

MF$_5$ (M = As, Sb; 3 mmol) was dissolved in HF/DF (ca. 5 g) in a KEL-F reactor. After freezing the solution H$_3$PO$_4$/(Me$_3$SiO)$_3$PO (3 mmol) was added under inert gas (N$_2$) at $-196\,^\circ$C. The reaction mixture was slowly warmed to $-60\,^\circ$C and kept at this temperature until a clear solution formed. The excess of HF, DF, and Me$_3$SiF was subsequently removed at $-60\,^\circ$C in a dynamic vacuum. P(OX)$_4^+$MF$_6^-$ (X = H, D; M = As, Sb) remained as a colorless solid that was stable up to $-10\,^\circ$C for M = As and $-3\,^\circ$C for M = Sb.

Analytical instruments: Raman: Jobin – Yvon T64000, Ar$^+$ laser (λ = 514,5 nm) Spectra Physics; IR: Bruker IFS 113v; NMR: Bruker DPX300; X-ray diffractometer: Nonius Mach 3.

[1] A. Hantzsch, *Chem. Ber.* **1925**, *58*, 941 – 961.
[2] D. R. Goddard, E. D. Hughes, C. K. Ingold, *J. Chem. Soc. London* **1950**, 2559 – 2575.
[3] E. J. Arlman, *Rec. Trav. Chim. Pays-Bas* **1937**, *56*, 919 – 922.
[4] A. Simon, M. Weist, *Z. Anorg. Allg. Chem.* **1952**, *268*, 301 – 326.
[5] C. C. Addison, J. W. Bailey, S. H. Bruce, M. F. A. Dove, R. C. Hibbert, N. Logan, *Polyhedron* **1983**, *2*, 651 – 656.
[6] R. C. Hibbert, N. Logan, *J. Chem. Soc. Dalton Trans.* **1985**, 865 – 866.
[7] R. J. Gillespie, R. Kapoor, E. A. Robinson, *Can. J. Chem.* **1966**, *44*, 1203 – 1210.
[8] K. B. Dillon, T. C. Waddington, *J. Chem Soc. A* **1970**, 1146 – 1150.
[9] G. A. Olah, C. W. McFarland, *J. Org. Chem.* **1971**, *36*, 1374 – 1378.
[10] M. Mathew, W. Wong-Ng, *J. Solid State Chem.* **1995**, *114*, 219 – 223.
[11] R. R. Holmes, R. N. Storey, *Inorg. Chem.* **1966**, *5*, 2146 – 2151.
[12] R. Schmutzler in *Advances in Fluorine Chemistry, Vol. 5* (Eds.: M. Stacey, J. C. Tatlow, A. G. Sharpe), Butterworth, London **1965**, pp. 134 – 140.
[13] R. Minkwitz, A. Kornath, W. Sawodny, *Angew. Chem.* **1992**, *104*, 648 – 649; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 643 – 644.
[14] R. Minkwitz, A. Kornath, W. Sawodny, *Z. Anorg. Allg. Chem.* **1994**, *620*, 753 – 756.
[15] R. Minkwitz, S. Schneider, M. Seifert, H. Hartl, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1404 – 1410.
[16] R. Minkwitz, S. Schneider, H. Preut, *Angew. Chem.* **1998**, *110*, 510 – 512; *Angew. Chem. Int. Ed.* **1998**, *37*, 494 – 496.
[17] R. Minkwitz, H. Hartl, C. Hirsch, *Angew. Chem.* **1998**, *110*, 1776 – 1779; *Angew. Chem. Int. Ed.* **1998**, *37*, 1681 – 1684.
[18] R. Minkwitz, S. Schneider, A. Kornath, *Inorg. Chem.* **1998**, *37*, 4662 – 4665.
[19] S. Gevrey, A. Luna, V. Haldys, J. Tortajada, J-P. Morizur, *J. Chem. Phys.* **1998**, *108*, 2458 – 2465.
[20] Crystal structure analysis of 1-SbF$_6$: crystals obtained from HF solution, monoclinic, space group C2/c (No. 15), a = 684.3(1), b = 783.5(1), c = 1426.6(2) pm, β = 95.47(1)$^\circ$, Z = 4, V = 761.4(2) × 10^6 pm^3; ρ_{calcd} = 2.920 g cm^{-3}, crystal dimensions: 0.22 × 0.14 × 0.14 mm^3, Mo$_{K\alpha}$ radiation (λ = 71.069 pm), 2θ/ω scans, 2θ_{max} = 65.0°, T = 193 K. Of the 2375 measured reflections, 1421 were independent, and 1134 were used in the refinement (σ to 2σ). Lp and absorption correction (ψ scans), μ(Mo$_{K\alpha}$) = 5.035 mm^{-1}, min/max transmission 0.78/0.91, structure solution method: Patterson, difference-Fourier-synthesis; SHELXS-86, SHELXL-93, PARST, PLATON, MISSYM, 64 free parameters, hydrogen atoms determined and refined experimentally from ΔF, R = 0.0206, wR = 0.0501, R = Σ||F_o|$-$|F_c||/Σ|F_o|, refinement method: full matrix least-squares on F^2; min./max. residual electron density = $-$1.073/0.501 e Å^{-3}. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (fax: (+49)7247-808-666; e-mail crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-408840.
[21] R. H. Blessing, *Acta Crystallogr. Sect. B* **1988**, *44*, 334 – 340.

Photochemistry of *ortho*-Phenoxymethyl-Substituted Aryl Azides: A Novel Nitrene Rearrangement En Route to Isolable Iminoquinone Methides?**

Götz Bucher* and Hans-Gert Korth

Aryl azides show a fascinating and complex photochemistry, which only recently could be elucidated in detail.[1–5] A singlet nitrene is formed as the primary reaction intermediate, which subsequently either adds intramoleculary to a neighboring C=C bond of the aromatic system,[1, 2] or relaxes to the ground-state triplet nitrene via intersystem crossing (ISC). The efficiency of spin inversion depends, among others, on the temperature and on the substitution pattern. Low temperatures favor ISC, and 2,6-bisubstitution retards addition to the C=C bond for steric reasons.[6] If only one *ortho* position is substituted, nitrene cycloaddition usually favors the unsubstituted side.[6] In the course of our own studies on ortho-substituted aryl azides we have synthesized 2,6-bis(phenoxy methyl)-1-azidobenzene **1**, and we have investigated its photochemistry by means of product analysis and matrix isolation spectroscopy.

Photolysis of **1**, which was matrix isolated in Ar at 10 K, yielded a new product **2** (Scheme 1). The UV/Vis spectrum of **2** is typical of a triplet aryl nitrene with a weak band in the visible part of the spectrum that extends to 530 nm, and sharp
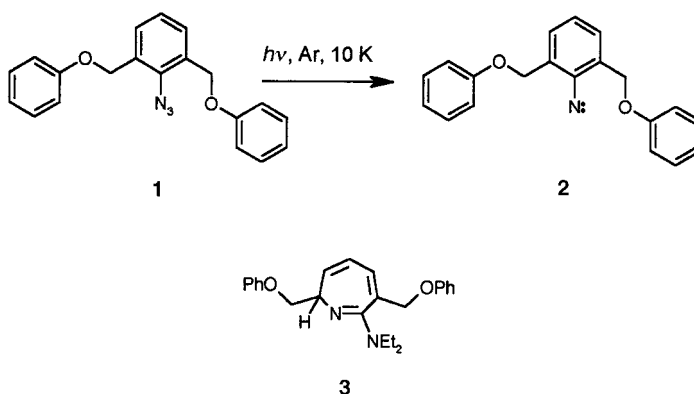
Scheme 1.

bands at 398, 296, and 288 nm (Figure 1). The infrared spectrum of **2** does not show bands that would be typical of products of nitrene rearrangement;[7] for instance, there are no bands at about 1890 cm^{-1} (typical for a didehydroazepine[2]). Photolysis of **1** is initially very efficient, but comes to a

[*] Dr. G. Bucher
Lehrstuhl OC II der Universität
Universitätsstrasse 150, D-44801 Bochum (Germany)
Fax: (+49) 234-709-4353
E-mail: goetz.bucher@orch.ruhr-uni-bochum.de

Dr. H.-G. Korth
Fachbereich 8—Chemie
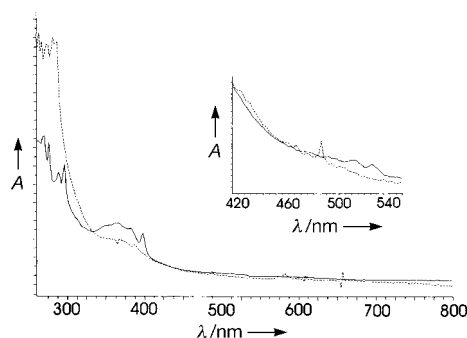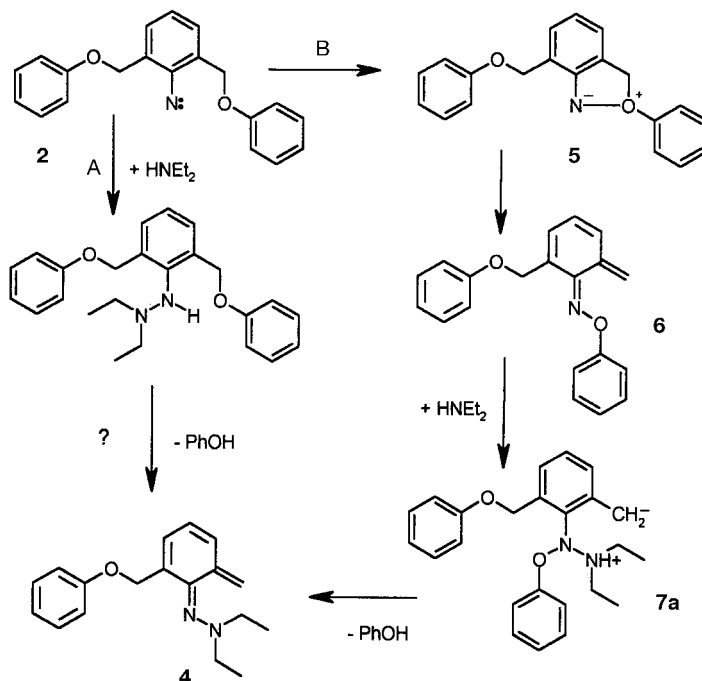Universität—Gesamthochschule Essen (Germany)

Figure 1. Solid line: UV/Vis spectrum of **2** obtained after photolysis (315 nm, 5 min) of **1** in an argon matrix at 10 K. Dashed line: UV/Vis spectrum obtained after photolysis (320 nm, 5 min) of **1** in glassy MTHF at 77 K. Inset: enlarged section between 420 and 540 nm. The spectrum obtained in MTHF at 77 K shows some sharp absorptions, which come from scattered light and are therefore artefacts.

standstill after a couple of minutes, presumably because of the filtering of light by **2**. Triplet nitrene **2** is essentially photostable at 10 K.[8] Contrary to this stability at 10 K, **2** is formed only in minute amounts if **1** is photolyzed in glassy 2-methyltetrahydrofuran (MTHF) at 77 K. The UV/Vis spectrum of the photolysate does not show the characteristic broad absorption of **2** with maxima at 512 and 526 nm (Figure 1), and the EPR triplet resonance at 6705 G ($g = 1.0145$) has only a very weak intensity.[9]

Photolysis (320 nm, 60 min) of **1** in CH_3CN/diethylamine (9/1) yielded 55 % of a yellow product after purification by column chromatography. Mass spectrometric analysis showed that the product was not the expected azepine **3**. Evaluation of the spectroscopic data revealed instead that the *syn* isomer of 6-*exo*-methylene-2-phenoxymethyl-cyclohexa-2,4-diene-1-on-*N,N*-diethylhydrazone **4** had been formed (Table 1). Of particular diagnostic value were the resonances $\delta(^{13}C) = 113.093$, as well as $\delta(^1H) = 4.9369$ (dd, 1H) and 4.9105 (d,

Table 1. NMR data for **4**.

$\delta(^{13}C)$	Assign-ment[a,b]	Couples with[a,b]	$\delta(^1H)$	Integral, multiplicity	J [Hz]
12.730	C14	H11	1.1033	6H, t	7.00
42.704	C13	H10	3.4504	4H, q	7.00
72.288	C5	H4	4.6722	2H, s	–
105.658	C7	H5	5.8169	1H, d	$J_{5,6} = 6.52$
113.093	C12	H8	4.9369	1H, d (dd?)	$J_{8,9} = 1.2$
		H9	4.9105	1H, d	(small)
115.168	C3	H3	6.9596	2H, d	$J_{2,3} = 7.52$
117.898	C9	H7	5.7774	1H, d	$J_{6,7} = 10.04$
120.399	C1	H1	6.8875	1H, t	$J_{1,2} = 7.16$
129.178	C2	H2	7.2287	2H, dd	$J_{2,3} = 7.52$
129.532	C8	H6	6.2007	1H, dd	$J_{5,6} = 6.54$, $J_{6,7} = 10.04$
136.573	C10	–	–	–	–
148.484	C6	–	–	–	–
149.017	C11	–	–	–	–
159.081	C4	–	–	–	–

[a] Based on GRAD-HMQC, COSY, and NOESY determinations. [b] The numbering of the carbon atoms starts in the 4-position of the phenoxy substituent, and proceeds clockwise in the molecule (see Scheme 2). Thus, C5 corresponds to the benzylic carbon atom, C11 to the imino carbon atom, and C12 to the *exo*-methylene carbon atom. The numbering of the hydrogen atoms is organized analogously.

1H). Their position and the fact that a GRAD-HMQC experiment showed cross peaks between these ^{13}C and ^1H resonances gave clear evidence for an *exo*-methylene group present in the molecule. The *syn* position of the diethylamino group, relative to the *exo*-methylene group, could be deduced from a NOESY experiment.

The iminoquinone methide **4** is a surprising product, whose formation necessitates the elimination of phenol. Two possible mechanisms for its formation will be briefly discussed (Scheme 2). In mechanism A the singlet nitrene inserts into

Scheme 2. Two routes to the formation of **4**.

the N–H bond of diethylamine. In a second step phenol is eliminated. However, **4** is formed almost exclusively. A ^1H NMR spectrum of the crude photolysate recorded after brief photolysis showed essentially only signals from **1** and **4**. Thus, any intermediary hydrazine derivative would have to be much shorter lived under the conditions of photolysis than **1**, which appears unlikely.[10] The first excited singlet state of aryl nitrenes is an open-shell state ($\sigma_1\pi_1$), which shows a high reactivity towards intramolecular rearrangement, but is difficult to intercept intermolecularly. Perfluorinated aryl nitrenes represent the only exception to this rule.[11] Photolysis of a series of 2-alkyl-substituted aryl azides did not lead to the formation of hydrazine derivatives,[12] and thus such a reaction appears unlikely in the case of **1**.

The primary reaction step in mechanism B is the formation of an oxonium ylide **5** (which may represent a transition state as well), which ring-opens to
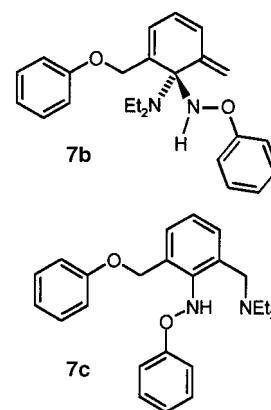
oxime **6**. Oxime **6** reacts with diethylamine to yield betaine **7a** (which may again be a transition state), which eliminates phenol to yield **4**. Alternatively, the reaction could also proceed via aminal **7b** or hydroxylamine **7c**. The mechanism via **7a** has some precedence in the literature: The reaction of iminoquinone methides **8** with secondary amines probably also proceeds via an addition–elimination-type mechanism (Scheme 3).[13] In this case, however, the negative charge in the betain resides on a nitrogen atom, and it is stabilized by an electron-withdrawing tosyl group. The formation of **7c** seems to be the most plausible possibility. However, the question remains why this compound should so readily lose phenol.
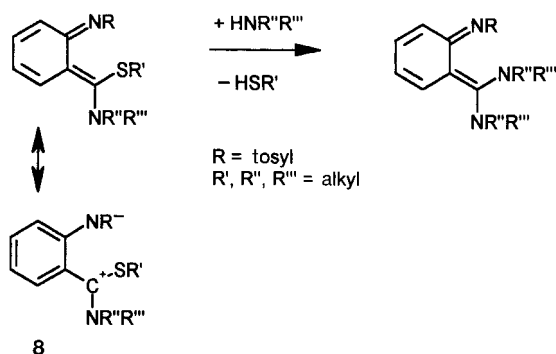
Scheme 3. Substitution of **8** through an addition–elimination mechanism.

The first singlet excited state of nitrene **2** is of unusual reactivity even at 77 K. This is also revealed by the fact that only a single phenoxymethyl group *ortho* to the nitrene center is required to obtain iminoquinone methides. Photolysis of azide **9** in the presence of diethylamine or piperidine allows for the isolation of the quinoid compounds **10** and **11**, again in approximately 50% yield (Scheme 4). As azepines are once again not formed as major products, the reaction that leads to **4** must have an activation barrier even lower than the very facile rearrangement to didehydroazepines.

The iminoquinone methides **4**, **10**, and **11** are isolable compounds of surprising stability (with half lives of the order of 24 h at ambient temperature and several weeks at $-18\,°C$). This observation is remarkable insofar as no isolable imino-quinone methides unsubstituted at the *exo*-methylene functionality had hitherto been known. Compounds of this type had up to now only been characterized by matrix isolation spectroscopy,[14, 15] or they were trapped in solution by Diels–Alder reactions.[16] The compounds **8** mentioned above bear donor substituents at the *exo*-methylene functionality as well as a tosyl acceptor substituent at the imino nitrogen atom, which results in push–pull stabilization.[13] Compounds **4**, **10**,

11: R = Et
12: R–R=(CH₂)₅
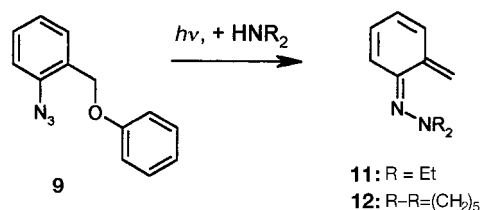
Scheme 4.

and **11**, however, only have a single donor substituent at the imino nitrogen atom and are otherwise stabilized only by steric protection by the *syn*-diethylamino group.

Experimental Section

General: All NMR spectra were recorded on a 400 MHz spectrometer with CDCl₃ as the solvent. The matrix isolation arrangement has already been described.[17] Photolyses at 77 K in glassy MTHF were performed with carefully degassed samples. The azides **1** and **9** were obtained from the corresponding aniline derivatives by diazotation and subsequent reaction with NaN₃.

4 (analogously **10** and **11**): A solution of **1** (50 mg) in CH₃CN/HNEt₂ (9/1, 40 mL) was purged with Ar for 15 min and then irradiated at $\lambda = 320$ nm for 60 min. (Quartz tube, photoreactor 400 with a UV radiator at 320 nm, Gräntzel, Karlsruhe, Germany). The solvent was then evaporated and the residue extracted with petroleum ether 60–80. The extract was purified by column chromatography (basic alumina, petroleum ether 60–80/triethyl-amine (98/2)) and **4** obtained as the first, yellow fraction. Additionally, some unphotolyzed **1** (20 mg) was recovered. Yield of **4**: 17 mg (55% relative to starting material consumed). UV (in CH₃CN): λ_{max} (ε) = 299 (16475), 279 (17500), 272 (17675), 222 (51700), 198 (51875); MS: m/z: 282 [M^+], 189 [M^+ – PhO], 118, 110, 91, 65; HR-MS: calcd: 282.173214; found: 282.173401. IR (film): $\tilde{v}$ = 2975 (m), 2933 (m), 1601 (s), 1562 (vs), 1524 (vs), 1498 (s), 1460 (m), 1429 (m), 1363 (m), 1295 (m), 1246 (m), 1220 (m), 1132 (m), 1080 (w), 1052 (w), 753 cm⁻¹ (s).

10: ¹³C NMR: δ = 149.4886, 141.2475, 136.7158, 118.5160, 113.0524, 108.9593, 42.5190, 12.6428; ¹H NMR: δ = 7.049 (d, 1 H), 6.204 (dd, 1 H), 5.794 (d, 1 H), 5.535 ("t", 1 H), 4.933 (s, 1 H), 4.909 (s, 1 H), 3.447 (q, 4 H), 1.108 (t, 6 H); IR (film): $\tilde{v}$ = 2976 (s), 2936 (s), 2873 (m), 1642 (w), 1591 (m), 1554 (vs), 1512 (vs), 1460 (m), 1429 (m), 1380 (m), 1363 (s), 1322 (m), 1297 (s), 1276 (w), 1232 (vw), 1137 (w), 1079 (s), 1011 (w), 901 (w), 783 (w), 732 (w), 683 cm⁻¹ (m); MS: m/z: 176 [M^+], 161, 147, 133, 120, 104, 94, 78, 65, 51.

11: ¹³C NMR: δ = 150.2926, 141.1013, 136.2956, 119.1373, 113.3631, 109.5806, 46.6121, 25.4521, 24.7395; ¹H NMR: δ = 6.985 (d, 1 H), 6.191 (dd, 1 H), 5.779 (d, 1 H), 5.542 (dd, 1 H), 4.939 (dd, 1 H), 4.898 (dd?, 1 H), 3.558 (t, 4 H), 1.60 (m, 2 H), 1.53 (m, 4 H); IR (film): 3013 (w), 2935 (s), 2855 (m), 1638 (w), 1590 (m), 1557 (vs), 1511 (vs), 1440 (s), 1368 (m), 1299 (s), 1280 (s), 1258 (w), 1238 (w), 1209 (s), 1130 (m), 1084 (m), 1062 (w), 1023 (m), 937 (w), 900 (m), 853 (w), 794 (w), 731 (w), 684 cm⁻¹ (w); MS: m/z: 188 [M^+], 173, 159, 145, 131, 119, 104, 79, 51, 41.

[1] E. Leyva, M. S. Platz, G. Persy, J. Wirz, *J. Am. Chem. Soc.* **1986**, *108*, 3783.

[2] C. J. Shields, D. R. Chrisope, G. B. Schuster, A. J. Dixon, M. Poliakoff, J. J. Turner, *J. Am. Chem. Soc.* **1987**, *109*, 4723.

[3] N. P. Gritsan, T. Yuzawa, M. S. Platz, *J. Am. Chem. Soc.* **1997**, *119*, 5059.

[4] R. Born, C. Burda, P. Senn, J. Wirz, *J. Am. Chem. Soc.* **1997**, *119*, 5061.

[5] W. L. Karney, W. T. Borden, *J. Am. Chem. Soc.* **1997**, *119*, 1378.

[6] W. L. Karney, W. T. Borden, *J. Am. Chem. Soc.* **1997**, *119*, 3347.

[7] IR bands assigned to the triplet nitrene **2** (Ar matrix, 10 K): $\tilde{v}$ = 1551 (m), 1515 (w), 1267 (m), 1250 (vs), 1240 (s), 1065 (w), 897 (w), 855 (w), 847 (w), 784 (s), 765 (s), 632 cm⁻¹ (m).

[8] Irradiation of **2** with a KrF excimer laser (248 nm) leads to the formation of bands at 2240 cm⁻¹, which may indicate a photochemical ring opening reaction.

[9] The intensity of this transition proved to be independent of the solvent. EPR spectra recorded with polycrystalline hexafluoroben-zene as the matrix material did not show more intense bands. For this reason the high reactivity observed for **2** (S₁) is probably not a consequence of reactions with the matrix material.

[10] Preliminary calculations (PM3/RHF) indicate, that the elimination of phenol from the hydrazine derivative formed by insertion of **2** in the N–H bond of diethylamine should be distinctly endothermic (by about 24 kcal mol⁻¹). A thermal elimination of phenol, as suggested by a referee, therefore seems unlikely. Such a reaction should also preferentially yield the *anti* isomers of the iminoquinone methides.

[11] H. Zhai, M. S. Platz, *J. Phys. Org. Chem.* **1996**, *10*, 22.

[12] R. J. Sundberg, S. R. Suter, M. Brenner, *J. Am. Chem. Soc.* **1972**, *94*, 513.

[13] R. Gompper, H. D. Lehmann, *Angew. Chem.* **1968**, *80*, 38; *Angew. Chem. Int. Ed. Eng.* **1968**, *7*, 74.

[14] W. Sander, J. Morawietz, *Tetrahedron Lett.* **1993**, *34*, 1913.

[15] J. Morawietz, W. Sander, M. Träubel, *J. Org. Chem.* **1995**, *60*, 6245.

[16] Y. Ito, E. Nakajo, T. Saegusa, *Synth. Commun.* **1986**, *16*, 1073.

[17] W. W. Sander, *J. Org. Chem.* **1989**, *54*, 333.

Formation and Structure of the First 7-Aza-1-phosphanorbornadiene Complex**

Udo Rohde, Frank Ruthe, Peter G. Jones, and Rainer Streubel*

Dedicated to Professor Edgar Niecke on the occasion of his 60th birthday

The chemistry of the norbornadienes (bicyclo[2.2.1]hepta-2,5-dienes) displays a variety of interesting aspects. One of these is the photochemical isomerization of norbornadienes to quadricyclanes[1] and its catalytic reversal.[2] Another is the synthesis, stability, and reactivity of heterocyclic analogues bearing a nitrogen or phosphorus atom at the 1- and/or 7-position (**I – III** in Figure 1); particularly noteworthy results from this area concern the differences in stability between 7-aza-[3] and 7-phosphanorbornadienes (Type **II**),[4] (the latter can be stabilized and isolated by coordination of the phosphorus to a metal[5]), and catalytic reactions[6] using 1-phosphanorbornadienes[7] (Type **I**) as novel ligands.
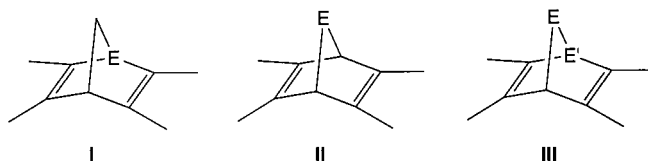

Figure 1. Heteronorborna-2,5-dienes **I–III** (exocyclic lines denote arbitrary substituents; E,E′ = N, NR and/or P, PR).

[*] Priv.-Doz. Dr. R. Streubel, Dipl.-Chem. U. Rohde,
Dipl.-Chem. F. Ruthe, Prof. Dr. P. G. Jones
Institut für Anorganische und Analytische Chemie
der Technischen Universität
Postfach 3329, D-38023 Braunschweig (Germany)
Fax: (+49) 531-391-5387
E-mail: r.streubel@tu-bs.de

Here we report the synthesis and structural characterization of a tungsten complex of the novel 7-aza-1-phosphanorbornadiene ring system.[8] This is formed by a trapping reaction of an intermediate, a PC₅Me₅-substituted nitrilium phosphane ylide tungsten complex,[9] with dimethylacetylene dicarboxylate (DMAD) and subsequent reaction with DMAD, which leads to cleavage of an exocyclic P–C bond. We also present a highly efficient synthesis of a novel phosphorus–carbon cage compound.[10]

If the 2H-azaphosphirene tungsten complex **1**[11] is heated in benzonitrile at 75 °C in the presence of DMAD, the 2H-1,2-azaphosphole tungsten complex **3** is formed (Scheme 1); however, **3** ($\delta(^{31}P) = 119.1$, $^1J(^{31}P,^{183}W) = 249$ Hz[9]) is not stable under these conditions, and undergoes cleavage of the exocyclic P–C bond (presumably by a radical mechanism) to form the transient intermediate 1H-1,2-azaphosphole complex **4**, which finally yields complex **5** by [4+2] cycloaddition with DMAD;[7, 12, 13] the source of the H atom is still unclear. Since this reaction also provided a product with a ³¹P NMR resonance signal at high field, ($\delta(^{31}P) = -66.8$, ca. 10%), we decided to repeat the reaction in toluene.[9] This led, after formation of a short-lived intermediate ($\delta(^{31}P) = -100.1$) to benzonitrile and, as sole phosphorus-containing product, the
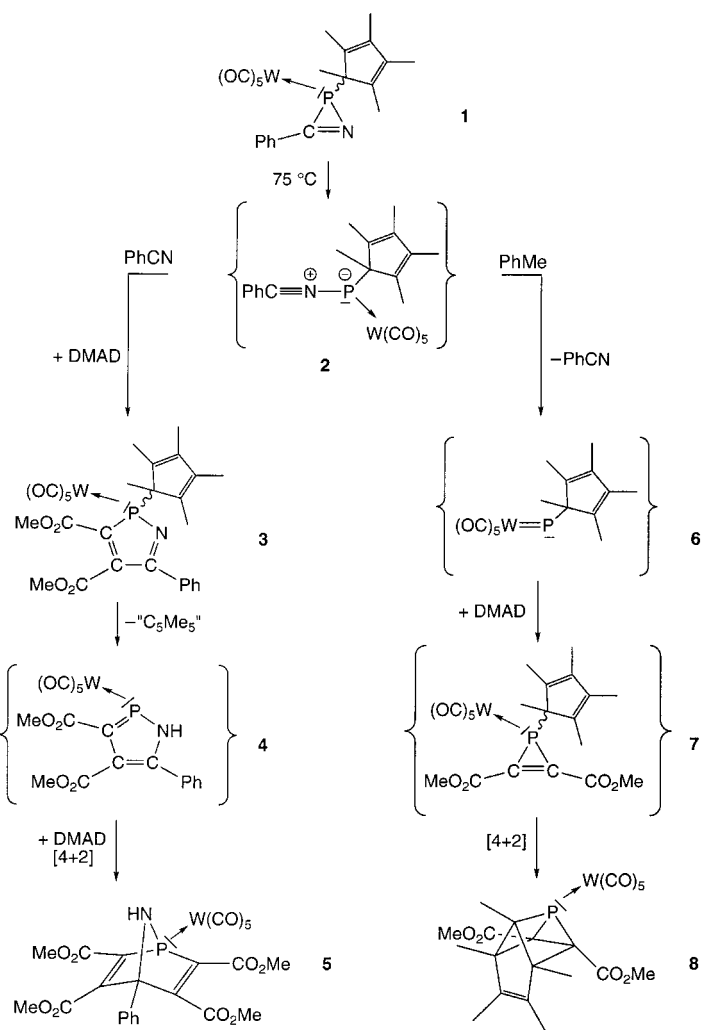
Scheme 1. Suggested reaction courses for the formation of complexes **5** and **8**.