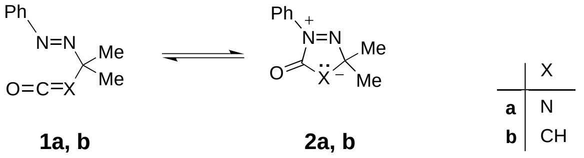
Azomethine Imines in Four- and Five-Membered Rings: Stable Cyclic Valence Isomers of an α-(Phenyldiazenyl)ketocarbene**

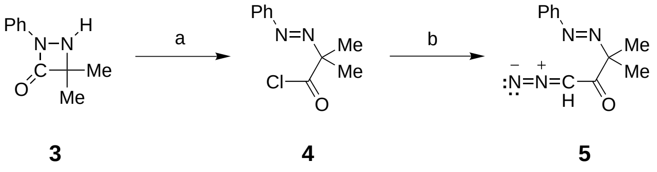
Joachim G. Schantl,* Arno S. Rettenbacher, and Klaus Wurst

The investigation of intramolecular interactions of functional groups and the resulting differences in reactivity constitutes a fascinating research area. For example, the reactivity of 1-(1-isocyanato-1-methylethyl)-2-phenyl-1-diazene (**1a**) is partly due to its cyclic valence isomer **2a**[1] (Scheme 1). The synthesis of 3-methyl-3-(2-phenyl-1-diazenyl)-1-buten-1-one (**1b**) was attempted in order to explore the extent to which the cyclic valence isomer **2b** might contribute to this reactivity.



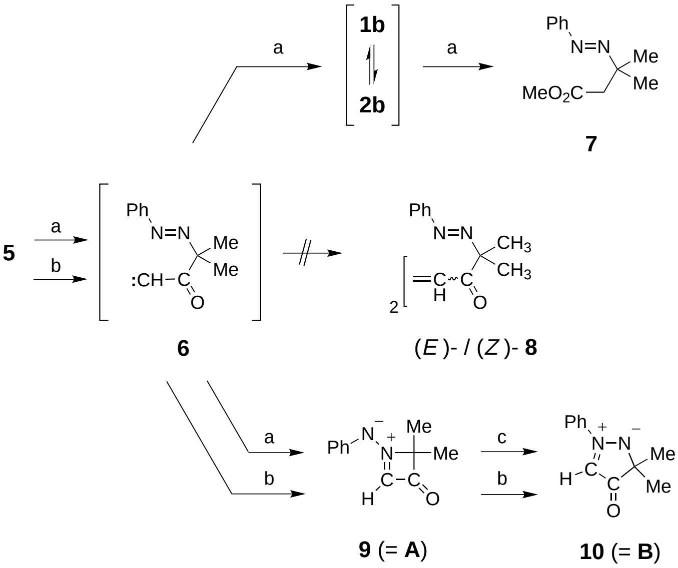
	X
a	N
b	CH

Scheme 1. Equilibrium between **1a** and its cyclic valence isomer **2a**[1] as well as the conceivable analogous isomerism between **1b** and **2b**.



Scheme 2. Synthesis of **5**: a) *t*BuOCl, CH_2Cl_2, 0 °C; b) CH_2N_2, Et_2O.

To this end, 4,4-dimethyl-2-phenyldiazetidin-3-one (**3**)[2] was transformed with *tert*-butyl hypochlorite into 2-methyl-2-(2-phenyl-1-diazenyl)propanoic chloride (**4**),[3] which in turn was treated with diazomethane to give 1-diazo-3-methyl-3-(2-phenyl-1-diazenyl)butan-2-one (**5**, Scheme 2). In the presence of methanol and under conditions which promote the Wolff rearrangement[4] diazoketone **5** extruded nitrogen to give two products: Methyl 3-methyl-3-(2-phenyl-1-diazenyl)butanoate (**7**) is the product expected from Wolff rearrangement to ketene **1b** via the ketocarbene **6** (Scheme 3). In addition, a second product **A** was isolated as light yellow crystals. The elemental analysis of **A** indicated the loss of dinitrogen from the starting material **5**. Transformation of **5** into **A** was faster in the presence of catalytical amounts of dimeric rhodium(II) acetate; however, under these conditions a 10:1 mixture of **A** and another yellow compound **B** was obtained. Compound **B** was also formed upon treatment of **5** with acetic acid at 70 °C as well as by acetic acid induced isomerization of **A** at 50 °C.



Scheme 3. Synthesis of **7** and **9**: a) CH_3OH, $C_6H_5CO_2Ag$, Et_3N. Synthesis of **9** and **10**: b) CH_2Cl_2, $[Rh_2(O_2CCH_3)_4]$, 0 °C. Isomerization of **9** to **10**: c) AcOH, N_2, 50 °C.

Heteronuclear multiple bond connectivity (HMBC) ^{13}C NMR experiments with **A** and **B** revealed the same carbon connectivity as in diazoketone **5**, thus ruling out structures **1b** and **2b**. The presence of an ion at *m*/*z* 377 in the fast atom bombardment (FAB) mass spectrum of **A** and **B** could be indicative of ketocarbene dimers (*E*)-**8** and (*Z*)-**8**, which are typical side products of reactions involving a ketocarbene intermediate.[4] The structure assignments of **A** and **B** were ultimately achieved by X-ray analyses:[5,6] **A** and **B** turned out to be *N*-(2,3-dihydro-2,2-dimethyl-3-oxo-1-azetio)phenylimide (**9**, Figure 1) and 3,4-dihydro-3,3-dimethyl-4-oxo-1-phe-

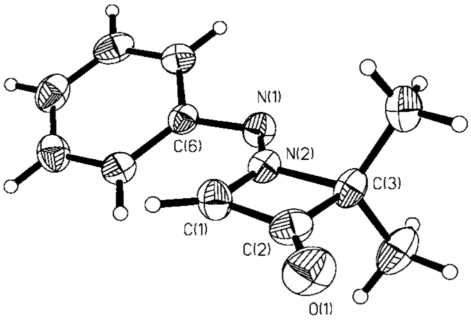


Figure 1. Molecular structure of **9** (thermal vibrational ellipsoids drawn at the 50 % probability level). Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.420(3), C(2)–C(3) 1.534(3), C(2)–O(1) 1.224(2), C(3)–N(2) 1.519(2), N(2)–C(1) 1.358(2), N(1)–N(2) 1.276(2), N(1)–C(6) 1.421(2); C(1)-C(2)-C(3) 91.2(2), C(2)-C(3)-N(2) 82.12(13), C(3)-(N2)-C(1) 94.28(14), N(2)-C(1)-C(2) 92.4(2), C(1)-C(2)-O(1) 136.8(2), O(1)-C(2)-C(3) 131.9(2), C(3)-N(2)-N(1) 123.3(2), N(1)-N(2)-C(1) 142.4(2), N(2)-N(1)-C(6) 117.6(2).

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nyl-2*H*-pyrazol-1-ium-2-ide (**10**, Figure 2), respectively. Both products are valence isomers of ketocarbene **6** and contain an azomethine imine functionality as part of a four-membered ring in **9** and a five-membered ring in **10**.

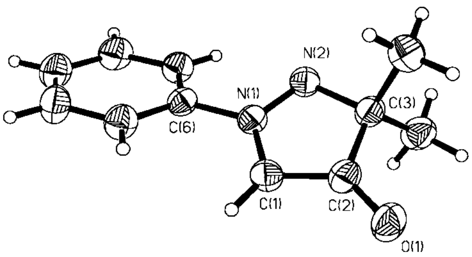

Figure 2. Molecular structure of **10** (thermal vibrational ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: C(l)–C(2) 1.402(3), C(2)–C(3) 1.516(3), C(2)–O(1) 1.246(2), C(3)–N(2) 1.468(3), N(2)–N(1) 1.303(2), N(1)–C(1) 1.351(3), N(1)–C(6) 1.449(3); C(1)-C(2)-C(3) 105.0(2), N(2)-C(3)-C(2) 105.9(2), C(3)-N(2)-N(1) 104.0(2), N(2)-N(1)-C(1) 118.5(2), N(1)-C(1)-C(2) 106.6(2), C(l)-C(2)-O(1) 130.0(2), O(1)-C(2)-C(3) 125.0(2), N(2)-N(1)-C(6) 118.2(2).

Crystal structure analyses of **9** and **10** revealed N–N bond lengths of 1.276(2) and 1.303(2) Å, respectively; both are greater than the length of N–N double bonds in typical diazenes (1.25 Å).[8] The endocyclic azomethine N–C bond lengths of 1.358(2) Å in **9** and 1.351(3) Å in **10** correspond well with those of delocalized systems (e.g. 1.34 Å in pyridine[8]). The C–O and C–C bonds (between carbonyl and azomethine carbon atoms) in the four-membered ring **9** (1.224(2) and 1.420(3) Å) are comparable to those of an α,β-unsaturated ketone (1.22 and 1.46 Å);[8] the corresponding distances in the five-membered ring **10** (1.246(2) and 1.402(3) Å) are indicative of some enolate contribution. Both heterocycles are planar, and the C–O and C–H bonds as well as the N–N (in **9**) and $N-C_{phenyl}$ bonds (in **10**) are in the plane of the respective heterocyclic rings; only the tetrahedral carbon atom of **10** is situated slightly above the plane defined by the four other ring members (dihedral angle 2.17(25)°). This deviation from planarity may be due to crystal packing, because the ^1H and ^{13}C NMR spectra show only one methyl signal. The significant difference of the ^{13}C NMR shift ($\Delta\delta \approx 20$) of the carbonyl groups of **9** und **10** is remarkable. The IR carbonyl frequencies of both compounds are distinctly different ($\tilde{\nu} = 1764$ and 1661 cm^{-1}, respectively, in $CHCl_3$), reflecting not only the different ring sizes but also some enolate contribution in **10**. The most intensive IR absorption of **9** at $\tilde{\nu} = 1514$ cm^{-1} (in $CHCl_3$) may be due to the vibration of the polar exocyclic N–N bond;[9] compound **10** is lacking a similar absorption of the endocyclic N–N bond.

The terminal carbon atom of the azomethine imine functionality of **9** and **10** is attached to a carbonyl group. Numerous examples of azomethine imines (open-chain, or partly or completely incorporated into a ring system) can be found in the literature.[10] However, the only known azomethine imines found within a four-membered ring are 1-methylen-3-oxo-1,2-diazetidin-1-ium-2-ides which have an exocyclic ylide carbon atom.[11] Thus, **9** represents a novel class of four-membered-ring azomethine imines with an exocyclic imide nitrogen atom. On the other hand, in **10** the azomethine imine functionality is completely embedded in the five-membered ring. The known analogues of this type of compound are sydnones;[12] thus, **10** represents the first example of a carba-sydnone in which the ring oxygen atom of a sydnone is replaced by a tetrahedral carbon atom. Although the mesoionic aromatic nature of sydnones is absent in **10**, this does apparently not alter the remarkable thermodynamic stability of azomethine imine **10**.

The isoelectronic character of diazene and carbonyl groups prompts a comparison between the α-(phenyldiazenyl)ketocarbene **6** (derived from diazoketone **5**) and β-carbonylketocarbenes which can be similarly generated in situ from β-carbonyl diazoketones. The formal analogy is perpetuated in the azomethine imine functionalities of **9** and **10** (the two stable valence isomers of ketocarbene intermediate **6**) and in carbonyl ylides, which are transient cyclic valence isomers of carbonyl ketocarbenes.[13] In the latter species, the oxygen atom of the carbonyl group is capable of interacting intramolecularly with the carbene center to form a carbonyl ylide with a five-membered ring as an interceptable dipolar intermediate. By contrast, both diazene nitrogen atoms of α-(phenyldiazenyl)ketocarbene **6** interact with the carbene center to afford both four- and five-membered azomethine imines. Apparently, valence isomer **9** is the kinetically controlled product; treatment with acid at 50–70°C induces its conversion into the thermodynamically more stable isomer **10**. Both novel azomethine imines **9** and **10** provide promising possibilities for further syntheses that are currently under investigation.

Experimental Section

4: To a stirred and ice-cooled solution of **3**[2] (2.0 g, 11.4 mmol) in absolute dichloromethane (30 mL) was added *tert*-butyl hypochlorite (1,9 g, 17 mmol). After 10 min the reaction mixture was evaporated in vacuo (0.005 mbar). Because of its tendency to decompose, the residual lachrymatory yellow oil **4** (2.4 g, 100%) was directly employed for the following reaction. $R_F = 0.75$ (silica gel; petroleum ether/diethyl ether 1/1). IR (film) $\tilde{\nu} = 3065$, 2990, 2937, 1793 (C=O) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.70$ (s, 6H; $2\,CH_3$), 7.46–7.54 (m, 3H; 2,4,6-H (C_6H_5)), 7.70–7.79 (m, 2H; 3,5-H (C_6H_5)); ^{13}C NMR (50 MHz, $CDCl_3$):[14] $\delta = 23.4$ (CH_3), 82.1 ($C-CH_3$), 122.6, 129.1, 131.5, 151.5, (3,5-, 2,6-, 4-, 1-C (C_6H_5)), 176.4 (C=O).

5: Dropwise addition of a solution of **4** (2.4 g, 11.4 mmol) in absolute diethyl ether (100 mL) to a stirred solution of diazomethane in diethyl ether (140 mL, ca 0.26 M) induced gas evolution. Excess of diazomethane and the solvent were removed in vacuo. The residual red oil was brought to crystallization by scratching at −100°C: orange crystals **5** (2.17 g, 88%), m.p. 43–45°C (pentane fraction), $R_F = 0.72$ (petroleum ether/diethyl ether 1/1). IR (KBr): $\tilde{\nu} = 3139$, 3065, 2986, 2935, 2154, 2103 (C=N=N), 1617 (C=O), 1460, 1374, 1354, 766, 695 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.47$ (s, 6H; $2\,CH_3$), 5.72 (s, 1H; HC–N),[15] 7.45–7.50 (m, 3H; 2,4,6-H (C_6H_5)), 7.68–7.74 (m, 2H; 3,5-H (C_6H_5)); ^{13}C NMR (50 MHz, $CDCl_3$):[14] $\delta = 22.9$ (CH_3), 53.6 (HC–N), 78.5 ($C-CH_3$), 122.3, 129.1, 131.0, 151.9 (3,5-, 2,6-, 4-, 1-C (C_6H_5)), 196.5 (C=O).

7 and **9**: To a stirred solution of **5** (0.5 g, 2.31 mmol) in absolute methanol (50 mL) were added ten drops of a solution of silver benzoate (1.0 g) in triethylamine (9.1 g) (Newman's reagent[16]). Gas evolution ceased after about 15 min, and a few more drops of the reagent were added, whereupon silver metal began gradually to deposit. Monitoring by thin-layer chromatography (TLC) indicated completion of the reaction after 2 h. The precipitate was filtered off, and the solvent was removed in vacuo from the filtrate. The residue was subjected to flash chromatography (silica gel (10 g), petroleum ether/diethyl ether 1/1) to afford two products:

Yellow oil **7** (0.28 g, 55 %), b.p. 100 °C (0.1 mbar); $n_D^{20} = 1.5520$; $R_F = 0.65$ (petroleum ether/diethyl ether 60/40). IR (film): $\tilde{\nu} = 3065$, 2986, 2935, 1738 (C=O), 1468, 1444, 1374, 1354, 1214, 772, 695 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.45$ (s, 6H; 2 CH_3), 2.77 (s, 2H; CH_2), 3.65 (s, 3H; OCH_3), 7.39 – 7.45 (m, 3H; 2,4,6-H (C_6H_5)), 7.60 – 7.67 (m, 2H; 3,5-H (C_6H_5)); ^{13}C NMR (50 MHz, $CDCl_3$):[14] $\delta = 25.1$ (C−CH_3), 44.0 (CH_2), 51.3 (OCH_3), 68.8 (*C*−CH_3), 122.0, 128.9, 130.2 152.0 (3,5-, 2,6-, 4-, 1-C (C_6H_5)), 171.9 (C=O).

Yellow crystals **9** (0.15 g, 35 %), m.p. 85 °C (petroleum ether); $R_F = 0.50$ (petroleum ether/diethyl ether 1/1); $R_F = 0.72$ (diethyl ether). IR (KBr): $\tilde{\nu} = 3114$, 3069, 2979, 2935, 1770 (C=O), 1751 (C=O), 1495, 1374, 1354, 772, 689 cm^{-1}; IR ($CHCl_3$): $\tilde{\nu} = 3030$, 3018, 1764 (C=O), 1514 (N=N), 804, 683 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 241 (3.79), 348 nm (4.31); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.70$ (s, 6H; 2 CH_3), 6.57 (s, 1H; HC−N), 7.20 – 7.30 (m, 3H; 2,4,6-H (C_6H_5)), 7.38-7.50 (m, 2H; 3,5-H (C_6H_5)); ^{13}C NMR (50 MHz, $CDCl_3$):[14] $\delta = 19.6$ (C−CH_3), 94.3 (*C*−CH_3), 117.8 (HC−N), 121.7, 127.1, 129.4, 147.4 (3,5-, 4-, 2,6-, 1-C (C_6H_5)), 184.5 (C=O); EI-MS (70 eV) *m*/*z* (%): 188 (38) [M^+], 133 (74) [M^+ − NCHCO], 118 (68) [$M^+ - Me_2C{=}C{=}O$], 91 (100) [$C_6H_5N^+$], 77 (60) [$C_6H_5^+$], 69 (63) [$HC{=}NCMe_2^+$], 42 (58) [$CH_2{=}CHCH_3^+$]; FAB-MS (NOBA): *m*/*z* (%): 377 (23) [$2M^+ + H$], 189 (100) [$M^+ + H$], 188 (29) [M^+]; elemental analysis calcd for $C_{11}H_{12}N_2O$: C 70.19, H 6.43, N 14.88; found: C 70.65, H 6.59, N 15.11.

10: Slow addition of **5** (1.0 g, 4.62 mmol) to a stirred solution of 98 % acetic acid (10 mL) at 5 °C induced a vigorous gas evolution and a strong exothermic reaction requiring efficient external cooling. After the gas evolution has ceased the mixture was stirred at 70 °C for 30 min before the solvent was distilled off in vacuo. The residue was dissolved in ether, the solution was washed with a saturated solution of sodium bicarbonate and with water until neutral, and dried over $MgSO_4$. The solid residue after removal of the solvent was recrystallized from petroleum ether/diethyl ether (1/1): dark yellow crystals **10** (0.69 g, 80 %), m.p. 100 °C, $R_F = 0.05$ (petroleum ether/diethyl ether 1/1). IR (KBr): $\tilde{\nu} = 3114$, 3069, 2973, 2922, 1636 (C=O), 1476, 1367, 759, 683 cm^{-1}; IR ($CHCl_3$): $\tilde{\nu} = 1661$ (C=O) cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 257 (3.85), 376 nm (3.71); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.44$ (s, 6H; 2 CH_3), 7.13 (s, 1H; HC−N), 7.50 – 7.64 (m, 3H; 2,4,6-H (C_6H_5)), 7.80 – 7.87 (m, 2H; 3,5-H (C_6H_5)); ^{13}C NMR (50 MHz, $CDCl_3$):[14] $\delta = 21.5$ (C−CH_3), 78.4 (*C*−CH_3), 113.7 (HC−N), 121.4, 129.6, 131.9, 140.9 (3,5-, 2,6-, 4-, 1-C (C_6H_5)), 204.2 (C=O); EI-MS (70 eV) *m*/*z* (%): 188 (43) [M^+], 104 (95) [$C_6H_5NCH^+$], 77 (100) [$C_6H_5^+$]; FAB-MS (NOBA): *m*/*z* (%): 377 (17) [$2M + H^+$], 189 (100) [$M + H^+$]; elemental analysis calcd for $C_{11}H_{12}N_2O$: C 70.19, H 6.43, N 14.88; found: C 70.37, H 6.55, N 14.97.

9 and **10** from **5**: To a stirred solution of **5** (0.5 g, 2.31 mmol) in dichloromethane (10 mL) at 0 °C was added [$Rh_2(O_2CCH_3)_4$] (< 1 mg), setting off a vigorous gas evolution. After 12 h the solvent was distilled off in vacuo at room temperature, and the residual oil was separated by flash chromatography (silica gel (10 g), diethyl ether) to provide **9** (0.39 g, 90 %) and **10** (0.04 g, 9 %).

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[5] a) Crystal structure analysis of **9** ($C_{11}H_{12}N_2O$, $M_r = 188.23$): crystal size 0.60 × 0.40 × 0.11 mm, monoclinic, space group *P*21/*c* (no. 14), $a = 12.337(1)$, $b = 6.823(1)$, $c = 12.263(1)$ Å, $\beta = 99.47(1)°$, $V = 1018.2(2)$ Å^3, $Z = 4$, $F(000) = 400$, $\rho_{calcd} = 1.228$ g cm^{-3}, $T = 213$ K; Siemens P4 diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), $\mu = 0.081$ mm^{-1}. Data were measured with ω scans and corrected for Lorentz and polarization effects; of 1081 reflections collected, 1017 were independent and 854 with $I \geq 2\sigma(I)$; structure solution by direct methods (SHELXS-86) and refinement against F^2 (SHELXL-93)[7] of 128 parameters with GOF = 1.058. Hydrogen atoms were placed in calculated positions. $R1 = 0.0306$ (against $|F|$), $wR2 = 0.0737$ (against $|F^2|$). b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100588. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[6] Crystal structure analysis of **10** ($C_{11}H_{12}N_2O$, $M_r = 188.23$):[5b] crystal size 0.60 × 0.30 × 0.28 mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 5.352(1)$, $b = 8.601(1)$, $c = 11.022(1)$ Å, $\alpha = 77.95(1)$, $\beta = 85.60(1)$, $\gamma = 84.96(1)$, $V = 493.38(12)$ Å^3, $Z = 2$, $F(000) = 200$, $\rho_{calcd} = 1.267$ g cm^{-3}, $T = 203$ K, $\mu = 0.083$ mm^{-1}. Data were measured with ω scans and corrected for Lorentz and polarization effects; of 1549 reflections collected, 1107 were independent and 972 with $I \geq 2\sigma(I)$. Structure solution by direct methods (SHELXS-86) and refinement against F^2(SHELXL-93)[7] of 128 parameters with GOF = 1.044; $R1 = 0.0396$ (against $|F|$), $wR2 = 0.1077$ (against $|F^2|$); max./min. residual electron density 0.168/ − 0.179 e Å^{-3}.

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