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N-Aminopyrroledione–hydrazonoketene–pyrazolium oxide–pyrazolone rearrangements and pyrazolone tautomerism†

Sieglinde Ebner,[a,b] Bianca Wallfisch,[a,b] John Andraos,[a] Ilyas Aitbaev,[b] Michael Kiselewsky,[a]
Paul V. Bernhardt,[a] Gert Kollenz[b] and Curt Wentrup*[a]
[a] *Department of Chemistry, School of Molecular and Microbial Sciences,*
The University of Queensland, Brisbane, Qld 4072, Australia. E-mail: wentrup@uq.edu.au
[b] *Institut für Chemie, Karl-Franzens-Universität Graz, A-8010 Graz, Austria*

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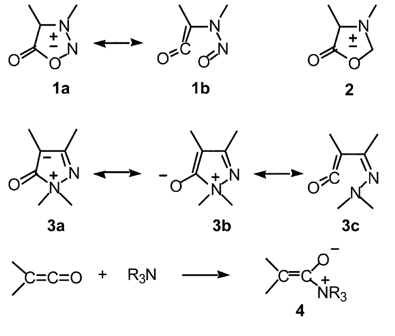
Flash vacuum thermolysis (FVT) of 1-(dimethylamino)pyrrole-2,3-diones **5** causes extrusion of CO with formation of transient hydrazonoketenes **7**. The transient ketenes **7** are observable in the form of weak bands at 2130 (**7a**) or 2115 cm^{-1} (**7b**) in the Ar matrix IR spectra resulting from either FVT or photolysis of either **5** or 1,1-dimethylpyrazolium-5-oxides **8**, and these absorptions are in excellent agreement with B3LYP/6-31G* frequency calculations. Under FVT conditions the ketenes **7** cyclize to pyrazolium oxides **8**, which undergo 1,4-migration of a methyl group to yield 1,4-dimethyl-3-phenylpyrazole-5(4*H*)-one **9a** and 1,4,4-trimethyl-3-phenylpyrazole-5(4*H*)-one **9b**. All three tautomers of **9a** have been characterized, *viz.* the CH form **9a** (most stable form in the gas phase, the solid state and solvents of low polarity), the OH form **9a′** (metastable solid at room temperature) and the NH form **9a″** (stable in aprotic dipolar solvents). The isomeric 1,4-dimethyl-5-phenylpyrazole-3(2*H*)-one **12** tautomerizes to the 3-hydroxypyrazole **12′**. The crystal structure of the hydrochloride **14** of **9a′**/**9a″** is reported, representing the first structurally characterised example of a protonated 5-hydroxypyrazole.

Introduction

The peculiar structures of the first mesoionic (mesomeric zwitterionic) compounds to be characterized, the sydnones[1] (1,2,3-oxadiazolium-5-olates) **1a**, revealed long endocyclic O–CO bonds (1.41 A) and large C4C5O angles (136°), which led to the suggestion of bond–no bond mesomerism with the ketene *resonance forms* **1b**.[1,2] Similar structures have also been reported for the münchnones (oxazolium-5-olates) **2**,[3] pyrazolium oxides **3** (*e.g.* N–CO = 1.55–1.57 Å; C4C5O = 140°),[4,5,6] and chromium complexes of pyrrolium-2-oxides (N-CO = 1.59 Å; C3C2O = 138.6°).[7] Pyrazolium and pyrrolium oxides can be formed by cyclization of transient hydrazono- or imino-substituted ketene intermediates,[6,7,8] and thus they can be regarded as cyclic ketene–amine zwitterions (see **4**).[9] However, in spite of much discussion and some circumstantial evidence, ketene *valence isomers* of these five-membered heterocycles have never been rigorously identified.[2] We have reported direct observation of such ring—chain valence isomers in another 5-membered mesoion series, *viz.* pyrrolo[1,2-*a*]pyridinium olates and (2-pyridyl)carbonylketenes.[10]



1,1-Dimethylpyrazolium-5-oxides of type **8** were first obtained from the reaction of ethyl benzoylacetate with *N*,*N*-dimethylhydrazine.[11] Subsequently, Chuche and co-workers[8] used flash vacuum thermolysis (FVT) of *N*,*N*-dimethyl-3-hydrazinopropenoates to generate transient *N*-(dimethylamino)-imidoylketenes, which cyclized to 1,1-dimethylpyrazolium-5-oxides. These compounds were isolable using reaction temperatures below 400 °C, but at higher temperatures they isomerised to 4,4-disubstituted pyrazole-5(4*H*)-ones, formally by 1,4-shifts of a methyl group from N1 to C4. 1,5-Alkyl shifts to give 1,2-dimethylpyrazolin-5-ones (antipyrine-type compounds) were not observed, nor were the presumed transient hydrazonoketenes detectable.

Results and discussion

We have prepared *N*-aminopyrrole-2,3-diones **5** by condensation of *N*,*N*-dimethylhydrazones of aromatic ketones with oxalyl chloride.[12] As with other pyrrole-2,3-dione derivatives,[13] FVT of **5** is expected to result in CO extrusion and formation of hydrazonoketenes **7**. In fact, FVT of the deeply red compound **5a** at 400 °C gave a product mixture which was separated by dry-column chromatography into the orange pyrazolium oxide **8a** and its rearrangement product, 1,4-dimethyl-3-phenylpyrazole-5(4*H*)-one **9a** (1 : 4)(Scheme 1). FVT of the hydrazone **6** at 600 °C (Chuche's method[8]) also resulted in a mixture of **8a** and **9a** (*ca.* 1 : 1) together with unchanged starting material **6** as established by GC-MS analysis. Moreover, compound **9a** was also obtained by FVT of **8a** at 500 °C. The IR and ^1H NMR spectra demonstrated that only traces of the known[14] antipyrine-type isomer **10a** were formed in these experiments. A plausible reason can be found in the thermochemistry: the calculated energy of **10a** is *ca.* 12 kcal mol^{-1} above that of **9a** at the B3LYP/6-31+G* level of theory.

The possible intermediates formed in the FVT reactions were investigated by matrix isolation IR spectroscopy. FVT of **5a** at 400 °C with isolation of the product in Ar matrix at *ca.* 10 K allowed the observation of a new band of weak intensity at 2130 cm^{-1} together with a strong band due to carbon monoxide (2139 cm^{-1}) and unchanged starting material **5a**. FVT at 700 °C resulted in formation of the rearrangement product **9a** (1732 cm^{-1}). The mesoion **8a** was barely detectable in these experi-

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† Electronic supplementary information (ESI) available: calculated and observed IR spectra of **8a** and X-ray structure, packing diagram, bond lengths and angles for compound **14**. See http://www.rsc.org/suppdata/ob/b3/b304070d

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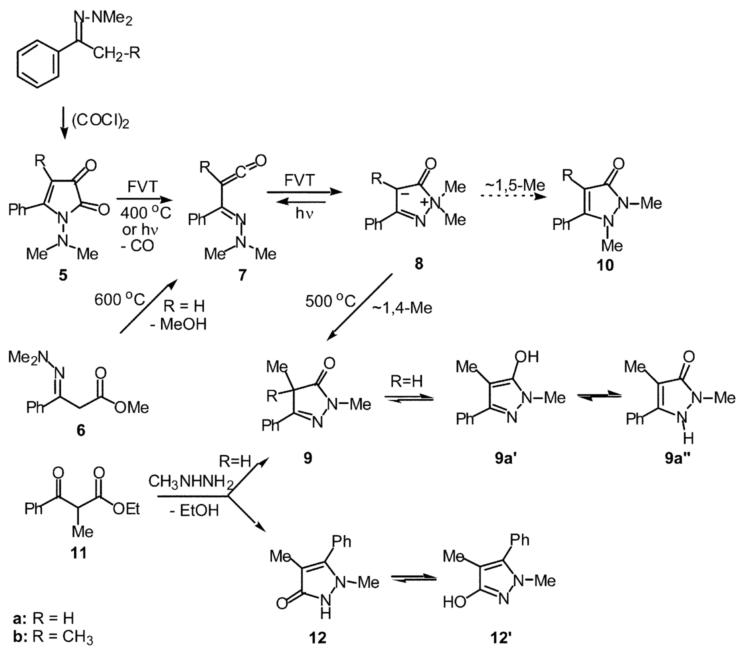


Scheme 1

ments, and FVT of **8a** itself (IR (Ar) 1771 cm^{-1}) at 500–665 °C resulted in the formation of **9a** (1732 cm^{-1}).

Photolysis of either **5a** or **8a** isolated in Ar matrices at 7 K also caused the development of a weak band at 2130 cm^{-1} in the IR spectra. It may be assumed that the absorptions at 2130 cm^{-1} are due to the transient hydrazonoketene **7a** (see below). In the photolysis of **8a** the amount of ketene doubled between 90 min and 4.5 h of irradiation, and this peak disappeared again after 7.5 h of irradiation. At this time the starting material (1771 cm^{-1}) had disappeared and been fully converted to **9a** (1732 cm^{-1}).

The 4-methylpyrroledione analog **5b** underwent similar thermolysis and photolysis reactions. However, **5b** sublimes very poorly, and so only low yields of FVT products and matrix-isolated materials can be obtained. The use of N_2 as a carrier gas and mixing of the starting material with finely powdered Cu improved the sublimation of this substance at 70 °C. The optimal FVT temperature was 400 °C. Even so, the amount of material subliming and undergoing FVT was only *ca.* 5%. The main product was identified as trimethylpyrazolone **9b**.

FVT of **5b** with Ar matrix isolation of the product at 7 K gave largely unchanged starting material, but at temperatures above 400 °C a new and weak peak at 2115 cm^{-1} appeared together with CO (2139 cm^{-1}) in the IR spectrum. Photolysis of this matrix, containing largely unchanged **5b**, resulted in an increase in the 2115 cm^{-1} peak, which may be ascribed to hydrazonoketene **7b**. The IR absorptions ascribed to **7a** (2130 cm^{-1}) and **7b** (2115 cm^{-1}) are in excellent agreement with the calculated values, 2133 and 2117 cm^{-1}, respectively. All other calculated vibrations are weak to very weak, and therefore it is not possible to identify any but the very strong C=C=O stretching bands in the experimental spectra. The good agreement and the fact that these bands are obtained both thermally and photolytically and from two different precursors (**5** and **8**) support their assignment to ketenes **7**.

A byproduct absorbing at 2259 cm^{-1} appeared in several of the FVT reactions of both **5a** and **5b**, particularly in the case of **5b**, and especially at high temperatures (*e.g.* 700 °C). The carrier of the 2259 cm^{-1} peak cannot be dimethylamino isocyanate (Me_2N–N=C=O), which absorbs at 2215 cm^{-1} in an Ar matrix.[15] Attendant bands at 3517, 3506 and 770 cm^{-1} identify the substance as isocyanic acid, HNCO.[16]

Mesoionic compounds usually exhibit ^{13}C NMR resonances at rather high field for the carbon atom that can formally carry the negative charge.[2,10] This is also true of the pyrazolium oxide **8a** (69 ppm for the vinylic CH carbon, C4) and other pyrazolium[6,8,17] and pyrrolium[18] oxides. The IR spectra of both six-membered (*e.g.* pyridinylium and oxazinylium olates[2]) and five-membered (*e.g.* münchnones[2] and pyrrolopyridinylium olates[10]) mesoionic compounds are very peculiar. Due to their highly polar character, the IR spectra in KBr and in Ar matrix are very different, with shifts in the range 30–60 cm^{-1} towards higher wavenumbers in the matrices.[2] In theoretical calculations of the IR spectra it is necessary to use diffuse functions on heavy atoms (6-31+G* basis set)[2] or to incorporate a simulated solvent field with a high dielectric constant (*e.g.* B3LYP/6-31G* calculation employing a self consistent reaction field (SCRF) with ε up to 40).[2] The use of diffuse functions is most effective. In the case of **8a** the C=O stretching vibration is found at 1733 (neat film)[11b] or 1730 and 1710 (KBr)[11a] cm^{-1}; we find 1735vs and 1710s cm^{-1} in KBr, and 1771vs cm^{-1} as the only strong band in the Ar matrix. As is often the case,[2] the B3LYP/6-31G* calculation predicts a C=O stretching vibration 37 cm^{-1} too high for the gas phase molecule (1808 cm^{-1}). The 6-31+G* basis set brings the predicted value (1769 cm^{-1}) into excellent agreement with experiment (1771 cm^{-1}) (see Fig. S1 in the electronic supplementary information †). We have used the same scaling factor (0.9613) for frequencies with the expanded 6-31+G* basis set as for the 6-31G* basis set; this may slightly underestimate the resulting frequencies. The high value of the C=O stretching frequency as well as the C4 chemical shift indicate that the enolate mesomer of **8** is not the dominant resonance structure. There is a significant degree of negative charge at C4 (*cf.* resonance structure **3a**), and a ketene-type 'no-bond' mesomer may contribute to the ground state of **8** as suggested by the X-ray data[4,5] (see structure **3c**). This is an example of the "structure-correlation principle" whereby the structure of a compound may presage the transition state for its formation or destruction, especially when the activation barrier is low.[19] In agreement with this, the calculated structure of **8a** features a very long CO–N bond (1.64 Å), a normal C=O bond (1.21 Å), a wide CCO angle (142°), an acute OCN angle (117°), and distances N–N = 1.45 Å, N–C(Ph) = 1.33 Å, C(Ph)–CH = 1.42 Å, and CH–CO = 1.39Å.

Tautomerism in pyrazolones

The calculated relative energies (B3LYP/6-31+G*; gas phase) of the isomeric molecules of interest (see Scheme 1) are as follows: **7a** (46.2), **8a** (25.4), **9a** (0.0), **9a′** (7.9), **9a″** (4.7), **10a** (11.6), **12** (7.5), **12′** (5.5 kcal mol^{-1}). These data predict that for **9a** the most stable form will be the CH-keto form, whereas the regioisomer **12** will exist preferably in the OH form **12′**. Our experimental data support this contention (see below). The structures and composition of tautomerizable pyrazolones–hydroxypyrazoles have been fraught with controversy and confusion.[20,21] In some cases, the hydroxy form predominates in the gas phase, in the solid state, and in nonpolar and dipolar aprotic solvents. Depending on substitution, the NH (keto) and CH forms may also participate in the equilibria. The proper identification of pyrazolone **9a** in the reactions above necessitated an unravelling of its tautomeric behaviour.

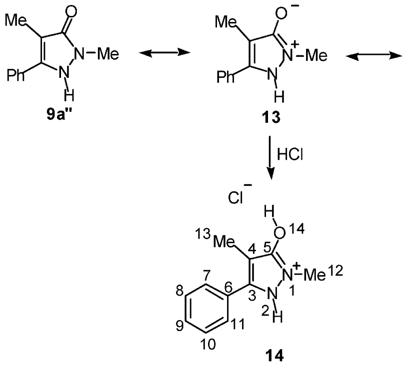
We repeated the original synthesis[22] of **9a** by reaction of β-ketoester **11** with methylhydrazine, separated the two products **9a** and **12**, and examined their structures by ^{1}H and ^{13}C NMR and IR spectroscopy. The IR spectra of **12** in Ar and Xe matrices demonstrate that this compound exists in the OH form **12′** (3615m, 1533s, 1517vs cm^{-1}). The crystalline solid in KBr also exists exclusively in the OH form **12′** (3200–2100s very broad hydrogen bonded OH; 1536vs, 1524vs cm^{-1}), and no carbonyl group is discernible in the IR spectrum. The experimental IR spectrum of **12′** is in excellent agreement with the B3LYP/6-31G* calculated spectra. The IR spectra of CCl_4 and $CHCl_3$ solutions are virtually identical with the one in KBr, and by far the major tautomer in these solvents must therefore be the hydroxy form **12′**, but the IR spectrum of the solutions in $CHCl_3$ and DMSO show an additional, very weak band near 1700 cm^{-1} which may be ascribed to a minor amount of the keto tautomer **12**. The ^{1}H and ^{13}C NMR spectra are essentially those of the OH tautomer **12′**. Adembri *et al.*[22] and Katritzky *et al.*[23] had assigned the NH structure **12** to this compound on the basis of the ^{1}H and ^{13}C NMR spectra, respectively.

The isomer **9a** is more complicated. In fact, all three tautomeric forms, **9a**, **9a″**, and **9a″** can be obtained selectively. To purify the compound, **12′** is best removed by recrystallization, and **9a** is then purified by chromatography on SiO_2. The solid compound so obtained, after removal of most of the solvent (ethyl acetate–methanol), is the enol form **9a′**, which shows a strong, broad signal for a hydrogen bonded OH group at 3200–2000 cm^{-1} but no C=O group in the IR (ATR and KBr). Because this compound tautomerises to **9a** on dissolution, an NMR spectrum cannot be obtained in solution. However, an excellent solid state ^{13}C NMR spectrum of **9a′** was obtained, and this shows good agreement with the calculated spectrum (B3LYP/6-31G*-GIAO).

After removing the solvent completely *in vacuo*, the compound isomerises to the pure keto form **9a** (C=O group at 1732 cm^{-1} in the Ar matrix IR spectrum; 175 ppm in the ^{13}C NMR spectrum). When dissolving the compound in CCl_4, it largely isomerises to **9a**, but a small amount of the enol form **9a′** is detectable in the initial IR spectrum. After 6 hours at room temperature, the compound has isomerised completely to the keto form **9a**. Sublimation or matrix isolation of the compound by vaporisation and co-condensation with Ar at 10 K affords only the keto form **9a**, which is calculated to be the lower energy isomer. Therefore, this is also the tautomer obtained in all FVT experiments.

When the compound is dissolved in DMSO-d_6, in contrast, the NH tautomer **9a″** is obtained. The IR spectrum and the ^{1}H and ^{13}C chemical shifts identify this tautomer as the NH form **9a″**, and they are in good agreement with the calculated spectra. The NH proton in **9a″** appears as a broad peak at *ca.* 10 ppm in DMSO-d_6 and with a very variable chemical shift in $CDCl_3$. The C=O group appears at 1696 cm^{-1} in the IR and at 149–150 ppm in the ^{13}C NMR spectrum. The reported ^{1}H and ^{13}C NMR spectra reveal that Adembri *et al.*[22] and Katritzky *et al.*[23] also observed **9a″**, in DMSO-d_6 and CD_3CN, respectively, but the former assigned the CH structure **9a** to it. Compound **9a″** is indefinitely stable in DMSO-d_6 solution, presumably due to H-bonding.

When the compound is dissolved in $CDCl_3$ that has been freed of any DCl contaminant by treatment with dry K_2CO_3, the NMR spectrum obtained is that of **9a** only. However, $CDCl_3$ usually contains varying amounts of DCl, and in such solutions, varying ratios of **9a** and **9a″** can be observed. Compound **9a″** can acquire aromaticity by existing in a zwitterionic mesomeric form **13**, which helps explain the low wavenumbers of the carbonyl groups in such compounds (≤ 1700 cm^{-1}). It has long been known that antipyrine (1,5-dimethyl-2-phenylpyrazol-3(2*H*)-one) and related compounds have very high dipole moments (of the order of 5.5 D), which imply large contributions by zwitterionic (mesoionic) resonance structures such as **13**.[24] Protonation of **13** on oxygen (or of **9a′** on N2) would generate a pyrazolium salt. In fact, **9a″** crystallizes from chloroform solution containing HCl (DCl) to form a salt **14**.



The single crystal X-ray structure of hydrochloride **14**‡ is shown in the electronic supplementary information (Fig. S2†). The sites of protonation were established unequivocally during refinement as being O14 and N2. Delocalisation (aromaticity) in the five-membered ring is apparent with bond lengths intermediate of single and double bond order (C–C (1.379(6) and 1.391(6) Å), C–N (1.326(5) Å and 1.346(6) Å) and N–N (1.352(5) Å). The C5–O14 and C4–C5 bond lengths (1.329(5) and 1.379(6) Å, respectively) are consistent with a hydroxypyrazole.[25,26,27] By contrast, pyrazol-5-ones in their keto form typically exhibit C–O and C–C bond lengths less than 1.28 and greater than 1.42 Å, respectively, with a wide range of distances reported according to the nature of substituents on the five-membered ring.[28,29]

A feature of the structure is an H-bonded chain extending along the direction of the *b* axis. The Cl ··· H-bonds involving the NH (H2 ··· Cl1 2.33(6) Å, N2 ··· Cl1 3.048(4) Å, N2-H2 ··· Cl1 170(6)°) and OH groups (H14 ··· Cl1′ 1.96(8) Å, O14 ··· Cl1′ 2.914(4) Å, O14–H14 ··· Cl1′ 162(6)°) are of comparable strength. The phenyl and pyrazole rings stack in a centrosymmetric dimeric array (Fig. S3†).

There are several examples of hydroxypyrazoles and pyrazol-5-ones with a substitution pattern similar to **14** in the Cambridge Structural Database.[30] However, **14** represents the first structurally characterized example of a 5-hydroxypyrazolium salt.

Computational details

Unless otherwise noted, all calculations were carried out at the B3LYP/6-31G* level of theory using the Gaussian 98 program package[31] and a scaling factor[32] of 0.9613 for frequencies. Energies of optimised geometries were calculated at both the B3LYP/6-31G* and B3LYP/6-31+G* levels. The differences in

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‡ CCDC reference number 207791. See http://www.rsc.org/suppdata/ob/b3/b304070d/ for crystallographic data in .cif or other electronic format.

energies obtained from the two basis sets were very minor, and only those from the B3LYP/6-31+G* calculations are reported. Zero point vibrational energy corrections are included. The data for the ketenes **7** refer to the *s-Z* conformers shown in Scheme 1 with *syn* configuration around the imine link (NMe$_2$ *syn* to the phenyl group). The *s-Z* and *s-E* conformers of imidoylketenes are usually very close in energy, and, depending on substituents, either conformer may be of lower energy.[33] Calculations on α-oxoketenes and imidoylketenes have been published previously.[34] For the vibrational data reported below, relative intensities are given in parentheses or as absolute values in km mol^{-1} where so indicated. NMR chemical shifts in ppm relative to TMS were calculated using B3LYP/6-31G*-GIAO. Peaks are listed in the numerical order of the corresponding atom numbers, and the following numbering is used: pyrazole ring: N1, N2, CO(3), C(Me)(4), C(Ph)(5); phenyl ring: atoms 6–11 (shifts for atoms 10–11 not listed); methyl groups: atoms 12 (on N) and 13 (on C). Hydrogen atoms are numbered as the heavy atoms they are attached to, OH is number 14, and the phenyl group hydrogens are not listed.

Relative energies. (B3LYP/6-31+G*; kcal mol^{-1}): **7a** (46.2), **8a** (25.4), **9a** (0.0), **9a′** (7.9), **9a″** (4.7), **10a** (11.6), **12** (7.5), **12′** (5.5). Absolute energy of **9a**: −610.905379 Hartree.

Infrared spectra. **7a** (*s-Z-syn* conformer shown): 2875 (16), 2133 (100; abs. int. 981), 1561 (12), 1381 (10), 1194 (3), 1046 (4), 974 (7), 685 (4), 644 (3), 535 (2) cm^{-1}.

7b (*s-Z-syn* conformer shown): 2874 (17), 2117 (100; abs. int. 846), 1559 (2), 1474 (2), 1346 (3), 1255 (5), 1201 (2), 998 (4), 763 (2), 685 (3) cm^{-1}.

8a: 3092 (1), 3081 (4), 3070(1), 3066 (1), 2970 (3), 2965 (1), 1808 (100), 1497 (2), 1480 (17), 1473 (2), 1462 (2), 1446 (1), 1433 (16), 1415 (2), 1406 (15), 1221 (2), 1183 (1), 1169 (1), 1127 (2), 987 (1), 955 (3), 913 (1), 811 (1), 716 (7), 683 (5), 655 (2), 650 (1), 615 (1), 595 (1), 572 (3), 615 (1), 511 (4) cm^{-1}.

8a (B3LYP/6-31+G*): 3090 (1), 3079 (3), 3062 (1), 2968 (2), 2963 (1), 1769 (100), 1491 (2), 1470 (15), 1468 (1), 1458 (1), 1441 (1), 1429 (12), 1400 (17), 1216 (12), 1181 (2), 1167 (1), 1130 (2), 952 (2), 911 (1), 808 (1), 716 (6), 679 (6), 654 (2), 616 (2), 605 (1), 572 (2), 521 (4) cm^{-1}.

9a: 2940 (14), 1743 (100), 1479 (60), 1226 (22), 1098 (15), 970 (9), 754 (7), 682 (6), 549 (6) cm^{-1}.

9a′: 3616 (43), 3079 (34), 2944 (42), 2902 (43), 1583 (50), 1564 (75), 1539 (64), 1441 (21), 1374 (100), 1290 (20), 1270 (22), 1231 (30), 1154 (61), 1003 (43), 691 (27), 220 (42), 196 (44) cm^{-1}.

9a″: 3329 (1), 3098 (1), 3089 (4), 3082 (4), 3071 (1), 2983 (7), 2977 (3), 2925 (13), 2920 (6), 1714 (100), 1619 (4), 1486 (2), 1457 (2), 1450 (2), 1436 (2), 1394 (7), 1359 (18), 1247 (9), 1226 (3), 1206 (2), 1158 (3), 1119 (2), 1050 (7), 980 (3), 807 (4), 796 (20), 755 (4), 734 (6), 706 (10), 686 (4), 617 (3), 595 (3), 286 (4) cm^{-1}.

9b: 3084 (8), 3011 (4), 2998 (5), 2941 (17), 1738 (100), 1478 (7), 1389 (4), 1379 (14), 1303 (6), 1287 (6), 1230 (26), 1033 (12), 1023 (5) 948 (6), 710 (7), 681 (7), 548 (8) cm^{-1}.

10: 3085 (3), 3009 (3), 2983 (6), 2926 (10), 2923 (8), 1723 (100), 1562 (4), 1481 (3), 1465 (3), 1348 (13), 1317 (11), 1228 (5), 1161 (5), 1121 (3), 788 (4), 753 (7), 687 (3) cm^{-1}.

12: 3435 (4), 1732 (100), 1609 (5), 1170 (10), 1134 (6), 994 (4), 750 (5), 736 (9), 509 (24) cm^{-1}.

12′: 3581 (26), 3082 (13), 2943 (28), 2922 (19), 1563 (11), 1516 (100), 1500 (23), 1484 (15), 1468 (12), 1299 (24), 1198 (30), 1158 (60), 1051 (14), 749 (15), 414 (29), 400 (21) cm^{-1}.

NMR spectra. **9a**: ^{13}C-NMR 163.9, 41.8, 151.6, 125.3, 120.0, 121.5, 122.2, 30.1, 17.1. ^{1}H NMR 3.0, 3.2, 1.3.

9a′: ^{13}C NMR 141.0, 87.6, 142.2, 128.8, 119.5, 120.5, 119.6, 34.4, 11.1. ^{1}H NMR 3.5, 1.9, 3.8.

9a″: ^{13}C NMR 158.3, 107.8, 145.1, 125.1, 122.6, 121.9, 122.4, 31.4, 10.7. ^{1}H NMR 4.5, 3.0, 1.9.

12: ^{13}C NMR 159.2, 109.3, 153.0, 125.2, 123.5, 121.8, 122.4, 39.8, 10.4. ^{1}H NMR 5.3, 2.6, 1.8.

12′: ^{13}C NMR 150.8, 95.4, 138.0, 125.8, 123.8, 121.7, 120.8, 35.1, 9.4. ^{1}H NMR 3.3, 1.8, 4.1.

Experimental section

General methods for flash vacuum thermolysis (FVT), matrix isolation and photolysis have been reported previously.[10,35] Ar matrix isolation experiments were done at 7–10 K. In preparative FVT experiments samples were sublimed into the thermolysis tube at 65–70 °C at a vacuum of *ca.* 2×10^{-4} mbar, and samples of **5** were sometimes mixed with Cu powder (1 : 1) to improve heat conductivity and sublimability. The unfiltered light from a 1000 W high pressure Hg/Xe lamp was used for the irradiations. GC-MS was recorded on a Hewlett-Packard instrument 5970 equipped with a BP5 capillary column (30 × 1.25 mm, phase thickness 0.25 mm); detector temperature 280 °C; column temperature programmed from 100 to 250 °C at 16° per minute. Melting points are uncorrected. IR spectra were obtained in Ar matrix, KBr, ATR (attenuated total reflexion) of solids, or in solution as indicated. ^{1}H NMR spectra were recorded at 400 or 200 MHz, and ^{13}C NMR spectra at 100 or 50 MHz. Chemical shifts are on the δ scale.

Crystallography

Cell constants were determined by least-squares fits to the setting parameters of 21 independent reflections measured on an Enraf-Nonius CAD4 four-circle diffractometer employing graphite-monochromated Mo Kα radiation (0.71073 Å) and operating in the ω-θ scan mode. Data reduction was performed with the WinGX package.[36] The structure was solved by direct methods with SHELXS and refined by full-matrix least-squares analysis with SHELXL-97.[37] All non-H atoms were refined with anisotropic thermal parameters. The H atoms attached to the N– and O-atoms were located from difference maps then refined isotropically. All other H-atoms were included in estimated positions using a riding model. A drawing of the molecule was produced with ORTEP[38] and the packing diagram was created with PLUTON.[39]

1,1-Dimethylamino-5-phenylpyrrole-2,3-dione 5a

A solution of 1.9 g (15 mmol) of oxalyl chloride in 2 mL of acetonitrile was added dropwise to a mixture of freshly prepared acetophenone *N,N*-dimethylhydrazone[40] (2.43 g; 15 mmol) and dry triethylamine (3.04 g; 30 mmol) in 20 mL of acetonitrile under N$_2$. The reaction is exothermic, and the addition rate should be such that no overheating occurs. The colour of the mixture changed from yellow to dark red, and a precipitate was formed. The mixture was stirred at 20 °C for 5 h, the precipitate was filtered, and the dark red solution was evaporated *in vacuo*. The resulting red oil was taken up in dry ether, and the solution was filtered and again evaporated *in vacuo*. Addition of 0.3 mL of dry ether and 1 mL of ether–hexane 1 : 1 caused crystallization with the aid of scratching. Yield: 0.65 g (20%); mp 81–82 °C; GC-MS R_t = 10.0 min; *m*/*z* 216 (4%), 188 (100), 173 (30), 145 (30), 116 (20), 102 (32), 86 (20), 57 (33), 43 (65); ^{1}H NMR (CDCl$_3$) 7.73–7.47 (m, 5H), 5.52 (s, 1H), 2.86 (s, 6H); ^{13}C NMR (CDCl$_3$) 181.3 (s), 171.4 (s), 150.0 (s), 132.6 (s), 129.0 (d), 128.5 (d), 127.8 (d), 99.5 (s), 44.0 (q). IR (Ar matrix, 8 K) 1764s, 1728vs cm^{-1}. Anal. Calcd for C$_{12}$H$_{12}$N$_2$O$_2$: C, 66.66; H, 5.59; N, 12.95. Found: C, 66.46; H, 5.85; N, 13.16%.

1,1-Dimethylamino-4-methyl-5-phenylpyrrole-2,3-dione 5b

This compound was prepared analogously to **5a** from propiophenone *N,N*-dimethylhydrazone. The dark red product was recrystallized from toluene–hexane to yield 1.86 g (54%); mp 146–148 °C; GC-MS R_t = 10.0 min; *m*/*z* 230 (10), 202 (100), 187

(34), 159 (70), 130 (34), 115 (34), 103 (20), 77 (31), 58 (28), 43 (70); ^{1}H NMR 7.51–7.42 (m, 5H), 2.80 (s, 6H), 1.74 (s, 3H); IR (Ar matrix, 8 K) 1756s, 1717vs cm^{-1}. Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.12; N, 12.53. Found: C, 67.41; H, 6.22; N, 11.98%.

1,1-Dimethyl-3-phenylpyrazolium-5-oxide 8a

This compound was prepared from **6** according to the literature.[11] GC-MS R_t = 9.5 min; *m*/*z* 188 (100%), 173 (26), 159 (16), 145 (23), 116 (13), 102 (29), 89 (10), 86 (19), 77 (39), 51 (30), 43 (62); IR (KBr) 1735vs, 1710s, 1458m, 700m cm^{-1}; IR (Ar, 10 K) 2951w, 1771vs, 1490m, 1450m (center of several bands), 1416m (center of several bands), 1254w, 1237w, 1199w, 1177w, 1147w, 1059w, 977w, 930w, 738m, 694m, 675w, 646w-m, 588m, 554w cm^{-1}; ^{1}H NMR ($CDCl_3$) 7.83–7.77 (m, 2H), 7.55–7.35 (m, 3H), 4.76 (s, 1H), 3.05 (s, 6H); ^{13}C NMR ($CDCl_3$) 178.8, 178.7, 131.5, 131.3, 128.6, 127.0, 68.9 (d), 47.9 (q).

1,4-Dimethyl-3-phenylpyrazol-5(4*H*)-one 9a, 1,4-Dimethyl-3-phenyl-5-hydroxypyrazole 9a′ and 1,4-Dimethyl-3-phenyl-pyrazol-5(2*H*)-one 9a″

Pyrazolone **9a** was prepared as the minor product of the reaction between methylhydrazine and **11** as described in the literature.[22] The compound was separated from **12′** by recrystallization of **12′** from benzene as described in the original preparation;[22] however, due to its toxicity, the use of benzene is discouraged. Flash chromatography on SiO_2 using gradient elution, starting with pure ethyl acetate and ending with ethyl acetate–methanol (ratio 4 : 1) followed by rapid and incomplete evaporation of the solvent gives the OH form **9a′**: IR (KBr) 3200–2000s v.br, 1586s, 1565s, 1540s, 1463m, 1449m, 1378m, 1293m, 1267m, 1251m, 1184m, 1047w, 771m, 697s cm^{-1}; IR (ATR) 3200–2100 v.br, 1584m, 1564m, 1537m, 696s; ^{13}C NMR (solid state) 152.4, 148.9, 131.3, 128.8 (several aromatic carbons), 91.7, 32.8, 5.6.

When the solvent is completely removed from **9a′** and the solid is dried *in vacuo* overnight, it tautomerises to the CH form **9a**. When the melting point of **9a′** is determined, the compound tautomerises to **9a**, mp 128–130 °C (lit.[22] 128–129 °C; lit[23] 130–132 °C).

Sublimation of the compound from the chromatography or generation by FVT of **5a** or **8a** with isolation in Ar matrix at *ca.* 10 K affords only the CH form **9a**: IR (Ar, 8 K) 1732s, 1475w, 1378w, 1347m, 1239m, 765w, 694m, 560w cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.46 (d, 3H), 3.39 (s, 3H), 3.54 (q, 1H), 7.40 (m, 2H), 7. 62 (m, 2H), 7.95 (m, 1H); ^{13}C NMR ($CDCl_3$) 175.68, 159.20, 129.75, 128.65, 127.17, 126.05, 42.74, 31.31, 14.49; GC-MS R_t = 8.5 min; *m*/*z* 188 (90), 173 (10), 159 (10),145 (40), 130 (22), 130 (21), 117 (100), 115 (69), 103 (95), 91 (35), 77 (69), 51 (65), 43 (40).

Dissolution of the solid from the chromatography in CCl_4 (not well soluble) also affords largely **9a**: IR (CCl_4) 1714s (a small amount of the enol **9a′** is detectable in the initial IR spectrum but has disappeared after 6 h at room temperature); ^{1}H NMR (CCl_4) 1.39 (d, 3H), 3.29 (s, 3H), 3.33 (q, 1H). ^{13}C NMR (CCl_4): 174.21, 158.84, 131.00, 128.24, 128.08, 127.24, 126.66, 41.89, 31.06, 14.50.

Dissolution of the solid from chromatography in DMSO-d_6 affords **9a″**: ^{1}H NMR (DMSO-d_6) 2.01 (s, 3H), 3.56 (s, 3H), 7.3–7.6 (5H), 10.0 (br s, 1H, variable shift); ^{13}C NMR (DMSO-d_6) 149.94, 146.16, 135.03, 128.23, 126.64, 126.38, 93.15, 33.49, 8.43. In DMSO-d_6 solution there is no tautomerization to **9a**; only the NH tautomer **9a″** is present. The calculated ^{13}C NMR spectra for **9a** and **9a″** are in good agreement with the experimental data.

A solution in pure $CDCl_3$ that has been treated with dry K_2CO_3 shows only **9a**: ^{1}H NMR ($CDCl_3$) 1.46 (d, 3H), 3.39 (s, 3H), 3.55 (q, 1H). In $CDCl_3$ containing traces of DCl a lesser amount of **9a** coexists besides (protonated) **9a″**: IR ($CDCl_3$/DCl) 1696s cm^{-1}; ^{1}H NMR ($CDCl_3$/DCl): 1.88 (s, 3H), 3.43 (s, 3H), 7.3–7.6 (5H), 9.0 (br, 1H, exchanges with D_2O, variable shift); ^{13}C NMR ($CDCl_3$/DCl): 148.76, 142.17, 133.47, 130.48, 128.81, 128.32, 101.76, 34.81, 8.25.

Pyrazolium salt 14. Compound **9a″** crystallizes from chloroform (deuterochloroform) containing HCl (DCl) to afford a hydrochloride **14**, mp 194–196 °C, the structure of which was determined by X-ray crystallography. Anal. Calcd for $C_{11}H_{13}N_2Cl$: C, 58.79; H, 5.84; N, 12.47. Found: C, 58.16;, H, 5.48; N, 12.39%.

Crystal data‡. $C_{11}H_{13}ClN_2O$, M = 224.68, triclinic, space group $P\bar{1}$, a = 7.348(2), b = 8.642(2), c = 9.832(3) Å, α = 103.70(2), β = 109.61(2), γ = 97.53(2)°, U = 556.1(3) Å^3, Z = 2, D_c = 1.342 g cm^{-3}, μ = 3.18 cm^{-1}, 2115 reflections measured, 1948 unique (R_{int} = 0.0423), R_1 = 0.0692 (for 1101 observed data, $I > 2\sigma$), wR_2 = 0.2244 (all data). Crystallographic data for compound **14** (in CIF format) have been deposited with the Cambridge Crystallographic Data Centre CCDC reference number 207791.

1,4-Dimethyl-5-phenylpyrazol-3(2*H*)-one 12 and 1,4-Dimethyl-5-phenyl-3-hydroxypyrazole 12′

This isomer is obtained as the major product of the reaction of **11** with methylhydrazine and purified by recrystallization from benzene (toluene).[22] The compound exists largely as the OH form **12′**: IR (Ar matrix, 7 K) 3615m, 1533s, 1517vs, 1328m, 1165s, 1014m 764m, 700m-s cm^{-1}; IR (KBr) 3200–2100s v.br, 1536vs, 1524vs cm^{-1}; IR (CCl_4) 3200–2100s v.br, 1537vs, 1522s cm^{-1}; IR ($CHCl_3$) 3200–2100 v.br, 1697vw, 1533s, 1520s cm^{-1}; IR (DMSO) 1709w, 1528s, 1509vs cm^{-1}; ^{1}H NMR ($CDCl_3$) 8 (br s, 1H; very variable chemical shift between 6 and 10 ppm), 7.47–7.40 (m, 3H), 7.34–7.24 (m, 2H), 3.61 (s, 3H), 1.91 (s, 3H); ^{1}H NMR (DMSO-d_6) 9.51 (s, 1H), 7.53–7.34 (m, 5H), 3.48 (s, 3H), 1.76 (s, 3H); ^{13}C NMR ($CDCl_3$) 160.0, 142.8, 130.0, 129.5, 128.6, 128.3, 98.8, 36.0, 6.85; GC-MS (**12** and/or **12′**) R_t = 8.8 min (broad); *m*/*z* 188 (100), 187 (90), 171 (3), 159 (6), 143 (10), 130 (7), 116 (8), 115 (33), 111 (28), 103 (5), 91 (8), 63 (7), 51 (10), 43 (7).

FVT of 5a

N-Aminopyrroledione **5a** was subjected to FVT at 400 °C with a sublimation temperature of 65 °C. The products were separated by dry-column chromatography on SiO_2 into **8a** and **9a** (1 : 4), which were identified by comparison with the NMR and IR data reported above. In addition, traces of **10a** were detected by its characteristic ^{1}H NMR signal at 5.6 ppm due to the methine proton.[14]

FVT of 6

The hydrazone **6** was subjected to FVT at 600 °C, and the products were analysed by GC-MS as a 1 : 1 mixture of **8a** and **9a** together with unchanged starting material **6**.

FVT of 8a

Mesoion **8a** was subjected to FVT at 500 °C with a sublimation temperature of 70 °C. **9a** was isolated by dry-column chromatography and identified by GC-MS, IR and ^{1}H NMR spectroscopy.

FVT of 5b

N-Aminopyrroledione **5b** was mixed with finely powdered Cu and subjected to FVT at 400 °C with a sublimation temperature of 70 °C. N_2 was used as a carrier gas at *ca.* 10^{-3} mbar. Due to the involatility of **5b** only *ca.* 5% of the material underwent FVT. The main product was separated by thick-layer plate chromatography and identified as 1,4,4-trimethyl-3-phenylpyrazol-5(4*H*)-one **9b** by its GC-MS behaviour and by comparison of its ^{1}H NMR spectrum with literature data.[8,41] GC-MS *Rt* 8.14 min; *m*/*z* 202 (100), 187 (22), 159 (30), 144 (20), 131 (80), 115 (45), 104 (30), 91 (46), 77 (36), 51 (31), 43 (32); IR (Ar, 8 K) 1728 cm^{-1}; ^{1}H NMR (CDCl$_3$) 7.85 (m., 2H), 7.65 (m, 3H), 3.30 (s, 3H), 1.38 (s, 6H).

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