



First Diels–Alder reaction of a N-nitrogen-substituted iminium ion as dienophile furnishing N-amino-substituted 1,2,5,6-tetrahydropyridines

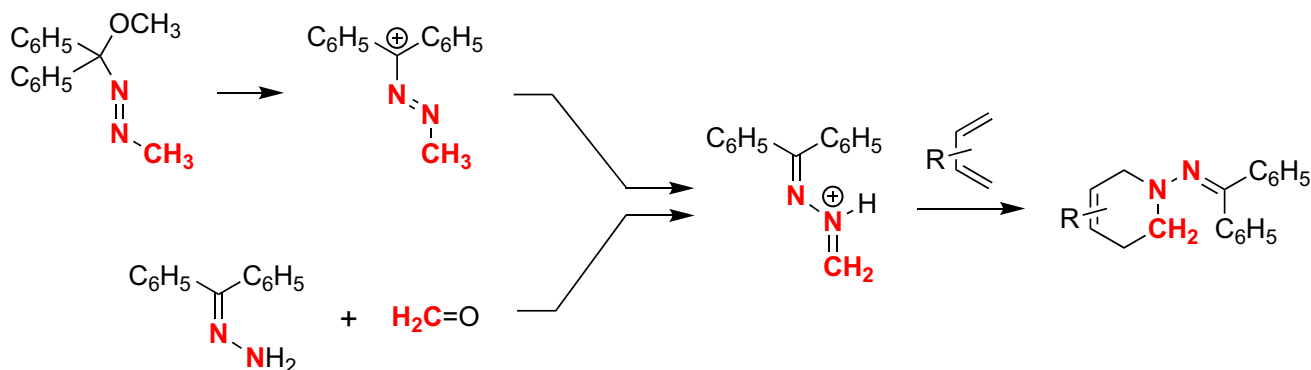
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Abstract

The exploratory and preliminary work on the reaction of 1-(methoxydiphenylmethyl)-2-methyldiazene with 1,3-dienes reveals a remarkable dichotomy furnishing different heterocyclic Diels–Alder products depending on the presence or absence of water. In contrast to the acid-induced hydrolysis of the N,O-ketal starting material with 1,3-dienes furnishing 1-methyl-1,2,3,6-tetrahydropyridazines (preceding communication), the same acid-promoted reaction albeit under exclusion of water affords *N*-(methyleneamino)-1,2,5,6-tetrahydropyridines. The serendipitous discovery of the novel 1,2,5,6-tetrahydropyridines was corroborated by an alternative and independent synthesis providing the in situ generated formaldehyde benzophenone azine and its conjugate acid, 2-(diphenylmethylene)-1-methylenehydrazin-1-ium ion. The protonated azine serving as the putative dienophile resembles the first example of an N-nitrogen-substituted iminium ion employed as a dienophile in a bona fide normal electron-demand Diels–Alder reaction.

Graphical abstract



Keywords [4 + 2⁺] Cycloaddition · 1-Methylene-1-hydrazinium ion · Heterodienophile · Hetero Diels–Alder · Heterocycles

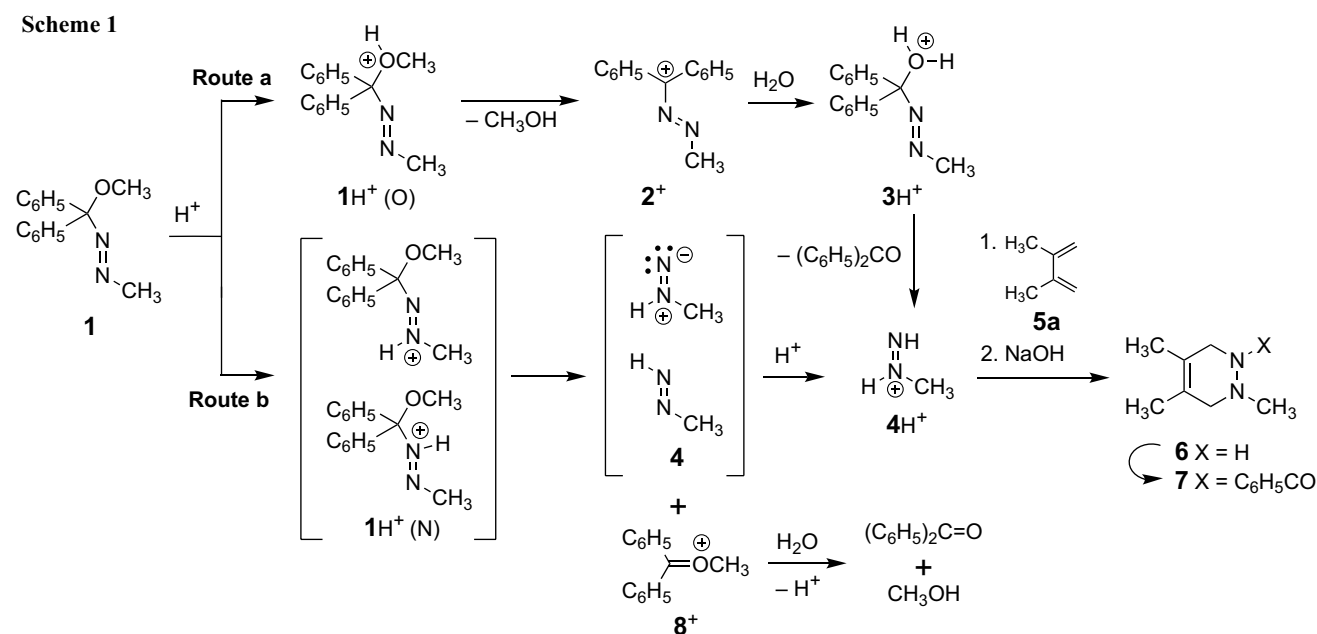
Introduction

As reported in the preceding communication [1], the acid-induced hydrolysis of 1-(methoxydiphenylmethyl)-2-methyldiazene (**1**) in the presence of 1,3-dienes affords 1-methyl-1,2,3,6-tetrahydropyridazine Diels–Alder products. Product formation is presumed via a sequence of putative intermediates (Scheme 1, route **a**): O-Protonation of hemiaminal methyl ether **1** forming the conjugate acid **1H⁺(O)** is

In memoriam of the dear friend and esteemed colleague Fritz Sauter.

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followed by dissociation resulting in 1-(diphenylmethylene)-2-methyldiazene-1-ium ion (2^+). In the presence of water intermediate 2^+ generates the protonated hemiaminal 3H^+ , which in turn decays furnishing 1-methyl-diazene-1-ium ion (4H^+) (as drawn, the structure 4H^+ is in keeping with the previous formulation [2]). Methyldiazanium ion 4H^+ reacting as dienophile, e.g., with 2,3-dimethyl-1,3-diene (**5a**) affords the Diels–Alder product 1,4,5-trimethyl-1,2,3,6-tetrahydropyridazine (**6**), which was transformed into the isolated *N*-benzoyl derivative **7**.

An alternative reaction sequence can be envisioned for the formation of dienophile 4H^+ (Scheme 1, route b). Protonation of the nitrogen atoms turns N,O-ketal **1** into two conjugate acids $1\text{H}^+(\text{N})$ depending on the protonation site. Dissociation of the N-protonated hemiaminal ethers $1\text{H}^+(\text{N})$ forms methyldiazene (**4**) (formulated as such and as the zwitterionic 2-methyldiazene-2-ium-1-ide isomer) along with cation 8^+ . Eventually, protonation converts methyldiazene (**4**, either form) into methyldiazanium ion (4H^+), and the reaction with diene **5a** furnishes the cycloadduct **6**.

The decisive difference between routes **a** and **b** in generating dienophile 4H^+ is the requirement of water in route **a**, whereas the reaction sequence outlined in route **b** is devoid of water; aqueous work-up merely hydrolyzes cation 8^+ .

Another conceivable way of forming cycloadduct **6** assumes that the two 1,2-dialkyl-substituted diazenium ions $1\text{H}^+(\text{N})$ may react as dienophiles and add to diene **5a**. However, this alternative can be disregarded because of the known lack of dienophilicity of 1,2-dialkyldiazenes and their conjugate acids (a notable exception based on a special structural feature of the azo compounds has been reported [3, 4]).

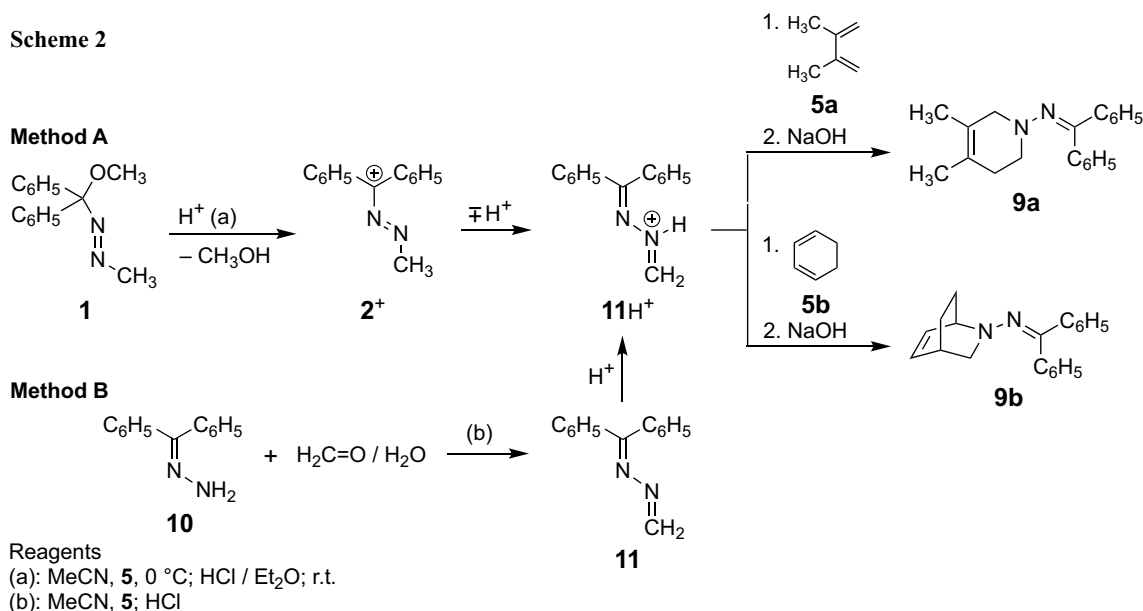
Experiments were designed to explore whether the acid-promoted reaction of **1** with dienes **5** under exclusion of water affords 1,2,3,6-tetrahydropyridazine Diels–Alder products like **6** (Scheme 1, route b).

Results and discussion

Reaction of N,O-ketal **1** and 1,3-dienes **5** with hydrogen chloride under exclusion of water—method A

The reaction of methyldiazanyl hemiaminal methyl ether **1** with 2,3-dimethyl-1,3-butadiene (**5a**) was carried out with a saturated solution of hydrogen chloride in dry diethyl ether under water-free conditions (Scheme 2, method A). Unexpectedly, the isolated product after work-up with aqueous sodium hydroxide solution did not prove to be cycloadduct **6**. Rather, a new product was obtained in modest yield (36%) and was found to be 3,4-dimethyl-1-diphenylmethyleamino-1,2,5,6-tetrahydropyridine (**9a**). The structure of product **9a** was confirmed by spectral data (^1H and ^{13}C NMR, DEPT, and COSY; Supplementary Material) as well as by an alternative synthesis (method B, vide infra) revealing that the product is composed of diene **5a** and 1-(diphenylmethylene)-2-methylenehydrazine (**11**). Taking into account that the reaction is carried out in the presence of acid, the conjugate acid of azine **11**, 2-(diphenylmethylene)-1-methylenehydrazin-1-ium ion (11H^+) appears to be the reactive N-nitrogen-substituted iminium ion dienophile in the $[4+2^+]$ cycloaddition reaction giving rise to the Diels–Alder product **9a**.

Scheme 2



Notably, in the product mixture of the acid-promoted water-free reaction of hemiaminal ether **1** with diene **5a**, the expected cycloadduct, 1,4,5-trimethyl-1,2,3,6-tetrahydropyridazine (**6**) was not detected. Conversely, in the acid-induced hydrolysis of N,O-ketal **1** with diene **5a**, the tetrahydropyridine Diels–Alder product **9a** has been identified as a by-product alongside tetrahydropyridazine **6** [1].

By the same water-free procedure, hemiaminal ether **1** and 1,3-cyclohexadiene **5b** afforded the corresponding Diels–Alder product, 2-(diphenylmethyleneamino)-2-azabicyclo[2.2.2]oct-5-ene (**9b**), also in a modest 36% yield.

Alternative preparation of 1-diphenylmethyleneamino-1,2,5,6-tetrahydropyridines **9**—method B

Inspired by the structure of cycloadducts **9** revealing their composition of the mixed azine **11** and the respective 1,3-diene **5**, an alternative synthesis was designed with the goal of further proving the structure of Diels–Alder products **9**.

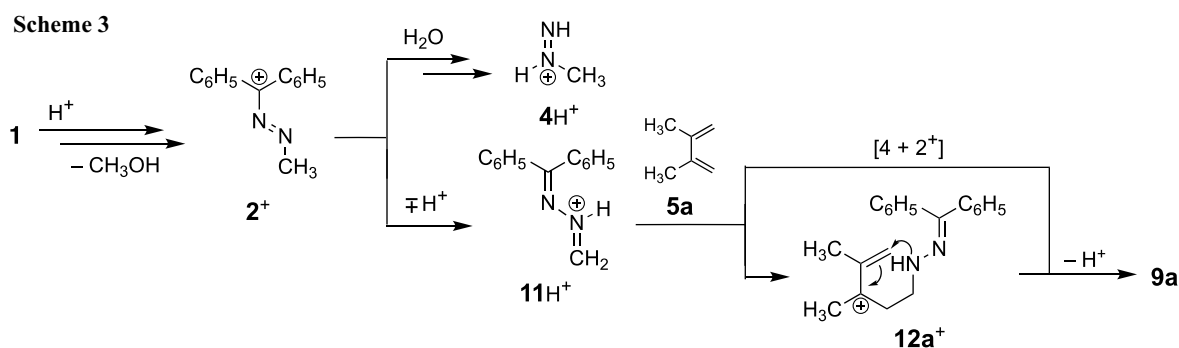
Analogous to the common practice of generating imines and iminium ions in situ by reacting primary amines with aldehydes in the presence of Brønsted acids [5–9], a bold one-pot reaction was chosen to provide the mixed azine **11**. To an acetonitrile solution of benzophenone hydrazone **10** and formalin (37% w/v formaldehyde in water) was added 2,3-dimethyl-1,3-butadiene (**5a**) and a solution of hydrogen chloride in diethyl ether (Scheme 2). Under the reaction conditions, the resulting azine **11** is converted into the conjugate acid **11H⁺**, and the protonated methyleneamine moiety is presumed to react as the N-nitrogen-substituted iminium ion dienophile with diene **5a**. Upon work-up with sodium hydroxide, yellowish crystals were obtained in 28% yield. Analytical and spectral data match those of Diels–Alder

product **9a** proving its identity. The same procedure was applied for the reaction of benzophenone hydrazone **10** with formaldehyde and 1,3-cyclohexadiene **5b** providing the bicyclic cycloadduct **9b** in 32% yield.

Reaction paths and intermediates

The acid-induced hydrolysis of methyldiazenyl hemiaminal methyl ether **1** in the presence of 1,3-dienes affords 1,2,3,6-tetrahydropyridazine Diels–Alder products [1], e.g., diene **5a** giving rise to cycloadduct **6** (Scheme 1, route a). Under exclusion of water, the acid-promoted reaction of N,O-ketal **1** with 1,3-dienes **5** affords only the novel Diels–Alder products **9** (Scheme 1, route b). The product mixtures were checked for cycloadducts like **6** and turned out to be devoid of those. This result clearly proves that the formation of 1,2,3,6-tetrahydropyridazine Diels–Alder products is exclusively following route a.

The noteworthy formation of different types of Diels–Alder products, 1,2,3,6-tetrahydropyridazines like **6** (and analogs [1]) and 1,2,5,6-tetrahydropyridines **9** from the same starting material, N,O-ketal **1**, is plausibly explained by the initial protonation of the methoxy group followed by dissociation, i.e., departure of methanol and formation of 1-(diphenylmethylene)-2-methyldiazen-1-ium ion (**2⁺**) (Scheme 3). Cation **2⁺** appears to be the common precursor of two subsequently formed intermediates, 1-methyldiazen-1-ium ion (**4H⁺**) and 2-(diphenylmethylene)-1-methylenehydrazin-1-ium ion (**11H⁺**), which in turn serve as the dienophiles in the reactions with dienes **5** furnishing Diels–Alder products like **6** and analogs [1] (Scheme 1, route a) and **9** (Scheme 2, method A), respectively.



Obviously, the cation intermediate **2⁺** is reactive in two ways. Water converts **2⁺** via the O-protonated hemiaminal **3H⁺** into dienophile methyldiazonium ion **4H⁺** (Scheme 1, route a; Scheme 3). Alternatively, cation **2⁺** is envisioned of undergoing a prototropy: loss of a proton from the methyl group forming the mixed azine **11** followed by protonation of the methanimine nitrogen atom forming the conjugate acid **11H⁺** (Scheme 3). Under exclusion of water, the acid-promoted reaction of **1** with dienes **5** (method A) appears to exclusively furnish dienophile **11H⁺**. On the other hand, dienophile **11H⁺** is also generated in the presence of water concomitantly and in competition with the formation of dienophile **4H⁺** as evidenced by the detection of cycloadduct **9a** as a by-product of **6** in the course of the acid-induced hydrolysis of **1** [1].

The mechanism of Diels–Alder reactions has long been controversial and there is growing evidence that certain $[4+2]$ cycloaddition reactions are better interpreted as stepwise processes, in particular, when the reaction is carried out with polarized or charged reactants or in the presence of Brønsted or Lewis acids [5, 10–15]. Therefore, the discussion of the formation of Diels–Alder products **9** based on a bona fide concerted cycloaddition reaction should be complemented by considering a stepwise process.

To account for an alternative stepwise reaction—exemplified for the reaction of diene **5a** with dienophile **11H⁺** on the way to product **9a** (Scheme 3)—an additional allyl cation intermediate **12a⁺** (or a transition state closely resembling it) may be considered. Nucleophilic addition of the diene methylene group onto the methaniminium ion moiety of **11H⁺** forms the carbon–carbon bond between the two methylene groups in cation **12a⁺**. Subsequent nitrogen–carbon bond formation initiated by the hydrazone NH-group of intermediate **12a⁺** closes the ring yielding product **9a**. However, making a definite statement about the mechanism of the reaction is beyond the scope of this work.

The serendipitous formation of Diels–Alder products **9** by the reaction of the in situ generated protonated azine **11H⁺** as an N-nitrogen-substituted iminium ion dienophile prompted a literature search about any predecessors.

N-nitrogen-substituted imines as dienophiles

Imines are probably the most widely utilized heterodienophiles in aza Diels–Alder reactions [5]. Among N-heterosubstituted imines, the range of N-nitrogen-substituted imines, i.e., hydrazones and azines, utilized as dienophiles is rather limited. Seitz et al. [16–19] described $[4+2]$ cycloadditions of dialkylhydrazones of aldehydes to the electron-deficient azine moiety of 1,2,4,5-tetrazines bearing electron-withdrawing substituents in 3,6-positions. Accompanied by extrusion of dinitrogen, the inverse electron-demand Diels–Alder reactions provide 4-(dialkylamino)-substituted 3,4,5,6-tetrahydro-1,2,4-triazines. Lewis acid activated aroylhydrazones of aldehydes have been reported to add to Danishevsky's diene affording 1-amino-2,3-dihydro-4-pyridone derivatives [20–22]. More recently, Danheiser et al. [23] investigated the reactivity of “unactivated” aldehyde dimethylhydrazones with “simple” 1,3-dienes like isoprene and ethyl sorbate (with thermal or Lewis acid activation). The reactions failed, thus confirming the relative lack of reactivity of dialkylhydrazones in conventional Diels–Alder reactions. In contrast, dimethylhydrazones participate as dienophiles in intramolecular $[4+2]$ cycloadditions with in situ generated, conformationally constrained and reactive vinylallenes [23].

Remarkably, only one example of an azine employed as dienophile has been reported, the reaction of hexafluoroacetone azine with 2,3-dimethyl-1,3-butadiene (**5a**). Tipping et al. [24] obtained two products arising from this reaction, a cyclic azomethineimine $[3+2]$ cycloadduct resulting from the 1,3-dipolar addition of the azine onto one of the olefinic bonds of the diene, and a formal $[4+2]$ cycloadduct featuring a N-(hexafluoropropan-2-imino)-1,2,5,6-tetrahydropyridine structure. Reexamining the formation of both products, Burger et al. [25] proved that the $[3+2]$ cycloadduct upon heating is converted into the $[4+2]$ cycloadduct by $[2,3]$ -sigmatropic rearrangement. The investigation of the temperature dependence of this conversion led to the conclusion that both the $[3+2]$ and the $[4+2]$ cycloaddition products may be arising concomitantly from competing reactions [25].

As a result, the herein reported Diels–Alder reaction involving the conjugate acid of benzophenone formaldehyde azine **11**, the 2-(diphenylmethylene)-1-methylenehydrazin-1-ium ion (**11H⁺**), appears to be the first example of an N-nitrogen-substituted iminium ion reacting as a heterodienophile.

Conclusion

In contrast to the acid-induced hydrolysis of 1-(methoxydiphenylmethyl)-2-methyldiazene (**1**) with 1,3-dienes **5** affording 1-methyl-1,2,3,6-tetrahydropyridazines like **6** [1], the same acid-promoted reaction albeit under exclusion of water yields the novel Diels–Alder products, *N*-(diphenylmethyleneamino)-1,2,5,6-tetrahydropyridines **9**. The remarkable dichotomy of N,O-ketal **1** giving rise to different heterocyclic products is explained by considering 1-(diphenylmethylene)-2-methyldiazin-1-ium ion (**2⁺**) as the common precursor of two presumed dienophiles on the way to the [4+2⁺] cycloadducts. Water is required for the transformation of cation **2⁺** into 1-methyldiazin-1-ium ion (**4⁺**), the putative dienophile in the reaction with diene **5a** yielding cycloadduct **6** [1]. Under exclusion of water, cation **2⁺** is converted into 2-(diphenylmethylene)-1-methylenehydrazin-1-ium ion (**11H⁺**), the dienophile in the reaction with dienes **5** affording *N*-(diphenylmethyleneamino)-1,2,5,6-tetrahydropyridines **9**. Diels–Alder products **9** were also readily obtained by an alternative and independent synthesis, the one-pot reaction of benzophenone hydrazone **10** with formaldehyde in the presence of 1,3-dienes **5** and acid, thus providing the mixed azine **11** and its conjugate acid **11H⁺**.—This exploratory and preliminary work expands the range of N-hetero-substituted imines and iminium ions serving as dienophiles in Diels–Alder reactions with the protonated azine **11H⁺** as the first example of a N-nitrogen-substituted iminium ion dienophile.

Experimental

Most reagents are commercially available from Fluka or Merck. The 1,3-dienes had a purity of >97%; 2,3-dimethyl-1,3-butadiene and 1,3-cyclohexadiene were stabilized with 0.1% hydroquinone and 0.1% 2,6-di-*tert*-butyl-4-methylphenol, respectively. All solvents were freshly distilled. Petroleum ether refers to the fraction of the boiling range 40–60 °C. Solvents were evaporated using a rotary evaporator Vapsilator (Chemphor) at ca. 2 kPa.

Thin-layer chromatography analyses were carried out on pre-coated polyester sheets with a silica gel layer, 4 × 8 cm (POLYGRAM SIL G UV254, Macherey–Nagel). Column chromatographic separations were performed as

low-pressure liquid chromatography (LPLC): glass columns (length 45 cm, i.d. 2.6 or 3.7 cm), silica gel 40–60 μm, 250 g (MERCK Kieselgel 60), external pressure 150–250 kPa.

Melting points were determined on a Kofler hot stage microscope (Thermovar-Reichert). The spectroscopic data have been obtained with the following instruments: Bruker AM 300 (¹H and ¹³C NMR, 300.13 and 75 MHz, respectively), Varian MAT 44S (MS).

Elementary microanalyses (C, H, N) were performed by Dr. J. Zak at the Institute of Physical Chemistry of the University of Vienna. The results are in good agreement with the calculated values.

(Diphenylmethylene)hydrazine (benzophenone hydrazone, 10) To a solution of hydrazine hydrate (98%, 40.75 cm³, 823 mmol) in ethanol (150 cm³) was added benzophenone (40.00 g, 220 mmol), and the mixture was refluxed for 24 h. Upon subsequent cooling in an ice-bath colorless crystals separated and were filtered off. The crystalline product was washed with diethyl ether yielding pure **10** (38.12 g, 88%); m.p.: 98–99 °C (lit. 98 °C [26]); *R_f*=0.54 (diethyl ether).

3,4-Dimethyl-1-(diphenylmethyleneamino)-1,2,5,6-tetrahydropyridine (9a, C₂₀H₂₂N₂) *Method A.* A solution of 1-(methoxydiphenylmethyl)-2-methyldiazene (**1**, 3.40 g, 14 mmol) [1] in anhydrous acetonitrile (20 cm³) was added within 15 min. to an ice-cooled, stirred mixture of 2,3-dimethyl-1,3-butadiene (**5a**, 20 cm³, 177 mmol), acetonitrile (30 cm³) and a saturated solution of hydrogen chloride in anhydrous diethyl ether (20 cm³). The resulting cloudy, yellow solution was stirred with continued ice cooling for 15 min and then without cooling for 50 min. Removal of the solvents and excessive diene **5a** in vacuo left behind a yellow oil (5.79 g), which was treated with 2 N sodium hydroxide (45 cm³). The resulting mixture was extracted with diethyl ether, the ether extract was dried (MgSO₄), and the solvent was removed in vacuo. To the oily residue (4.40 g) was added 2 N hydrochloric acid (40 cm³), and the aqueous phase was repeatedly extracted with diethyl ether (6 × 50 cm³). The combined ether extracts were dried (MgSO₄), and the solvent was removed under reduced pressure to give a yellow–brown oil (3.68 g) that turned crystalline upon standing. Work-up by LPLC (silica gel, diethyl ether/petroleum ether 1:6) provided yellowish crystals **9a** (1.44 g, 36%). M.p.: 79–80 °C (ethanol/water); *R_f*=0.44 (diethyl ether/petroleum ether 1:6); ¹H NMR (300.13 MHz, DMSO-*d*₆): δ = 1.48 (s, 3H, 3-CH₃), 1.57 (s, 3H, 4-CH₃), 1.93 (br s, 2H, 5-CH₂), 2.91 (t, *J* = 8.8 Hz, 2H, 6-CH₂), 3.27 (br s, 2H, 2-CH₂), 7.22–7.50 (m, 10H, 2 C₆H₅) ppm; ¹³C NMR (75.47 MHz, DMSO-*d*₆): δ = 16.1 (CH₃), 17.8 (CH₃), 30.5 (5-CH₂), 51.4 (6-CH₂), 58.3 (2-CH₂), 122.8, 123.9, 127.1, 127.8, 128.2, 128.3, 128.7, 136.6, 139.1 (= CH, C₆H₅), 155.3 (C = N) ppm; EI-MS: *m/z* (%) = 290 (10.50,

M⁺), 207 (16.30), 182 (36.59), 181 (15.57), 180 (17.93), 165 (10.32), 110 (11.41), 109 (12.31), 108 (10.68), 106 (10.50), 105 (100), 104 (22.64), 77 (68.11), 51 (35.86), 45 (24.09), 43 (44.56), 42 (24.81), 41 (29.89).

The acidic aqueous phase was worked-up with 2 N NaOH and benzoyl chloride but 1-benzoyl-2,4,5-trimethyl-1,2,3,6-tetrahydropyridazine **7** [1] was not detected.

Method B. To a mixture of benzophenone hydrazone (**10**, 3.92 g, 20 mmol), formalin (37% w/v formaldehyde in water, 5.0 cm³, 61 mmol), and acetonitrile (40 cm³) was added 2,3-dimethyl-1,3-butadiene (**5a**, 6.0 cm³, 53 mmol). Thereafter, a saturated solution of hydrogen chloride in diethyl ether (20 cm³) was added causing the solution to turn yellow-orange. After removal of the solvent and excessive diene **5a** in vacuo the residual oil was basified with 2 N sodium hydroxide (50 cm³) and repeatedly extracted with diethyl ether. The ether extracts were combined, dried (MgSO₄), and the solvent was removed in vacuo. The residual brown oil was worked-up by LPLC as described above affording yellowish crystals **9a** (1.64 g, 28%).

2-(Diphenylmethyleneamino)-2-azabicyclo[2.2.2]oct-5-ene (**9b**, C₂₀H₂₀N₂)

Method A. A solution of 1-(methoxydiphenylmethyl)-2-methyldiazene (**1**, 2.40 g, 10 mmol) [1] in anhydrous acetonitrile (15 cm³) was combined under stirring with an ice-cooled solution of 1,3-cyclohexadiene (**5b**, 5.0 cm³, 52 mmol) in acetonitrile (15 cm³). Subsequently, a saturated solution of hydrogen chloride in anhydrous diethyl ether (17 cm³) was added drop-wise within 10 min and stirring was continued until the resulting yellow-orange solution warmed up to ambient temperature. After distilling off the solvents and excessive diene **5b** under reduced pressure, the residual brown oil was basified with 2 N sodium hydroxide (25 cm³). Extraction with diethyl ether, washing the ether phase with 2 N hydrochloric acid followed by repeated washing with water until neutral, drying (MgSO₄), and removal of the organic solvent in vacuo afforded a red-brown oil (2.25 g). Purification by LPLC (silica gel, ether/petroleum ether 1:2) provided a yellowish crystalline product, which after recrystallization from methanol gave colorless crystals **9b** (1.04 g, 36%). M.p.: 78–79 °C (methanol); R_f = 0.79 (diethyl ether/petroleum ether 1:2); ¹H NMR (300.13 MHz, CDCl₃): δ = 1.15–1.25, 1.32–1.38, 1.38–1.50, 2.13–2.19 (m, 4 × 1H, CH₂CH₂), 2.13–2.17 (m, 1H, 3-CH_A), 2.19–2.23 (m, 1H, 3-CH_B), 2.35–2.41 (m, 1H, 4-CH), 4.21–4.27 (m, 1H, 1-CH), 6.36–6.42 (m, 1H, =CH), 6.51–6.57 (m, 1H, =CH), 7.20–7.40 (m, 10H, 2 C₆H₅) ppm; ¹³C NMR (75.47 MHz, CDCl₃): δ = 21.9 (CH₂), 24.8 (CH₂), 32.2 (4-CH), 57.3 (1-CH), 61.4 (3-CH₂), 133.1 (=CH), 133.13, 133.16 (=CH), 127.4–129.9, 138.8, 140.8 (C₆H₅), 146.7 (C=N) ppm; EI-MS: m/z (%) = 288 (39.72, M⁺), 287 (19.44), 260 (24.16), 259 (31.38), 258 (14.16), 209 (16.66), 208 (16.38), 207 (33.05), 206 (18.88), 181

(18.88), 180 (100), 179 (80.55), 178 (29.72), 164 (30.38), 163 (10.83), 105 (12.50), 104 (18.61), 80 (36.11), 70 (40.27), 78 (29.44), 77 (65.55).

2-Benzoyl-3-methyl-2,3-diazabicyclo[2.2.2]oct-5-ene [1] was not detected upon work-up of the acidic aqueous phase with 2 N NaOH and benzoyl chloride.

Method B. To the solution of benzophenone hydrazone (**10**, 1.96 g, 10 mmol), formalin (37% w/v formaldehyde in water, 3.0 cm³, 37 mmol), and 1,3-cyclohexadiene (**5b**, 4.0 cm³, 42 mmol) in acetonitrile (20 cm³) a saturated solution of hydrogen chloride in diethyl ether (10 cm³) was added. The solvent and excessive diene **5b** were distilled off at reduced pressure. The residual oil was treated with 2N sodium hydroxide (50 cm³) and repeatedly extracted with diethyl ether. After drying the combined extracts (MgSO₄) and removing the solvent in vacuo, a yellow oil (2.66 g) was obtained, which upon purification by LPLC (silica gel, diethyl ether/petroleum ether 1:9) afforded colorless crystals **9b** (0.90 g, 32%).

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00706-023-03054-7>.

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