# The Thermolysis of the Cycloadducts between Aryl Azides and Hexamethyl-*Dewar*-Benzene Revisited

by **Manfred Christl*** and **Steffen Lesch**

Institut für Organische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg
(e-mail: christl@chemie.uni-wuerzburg.de)

and

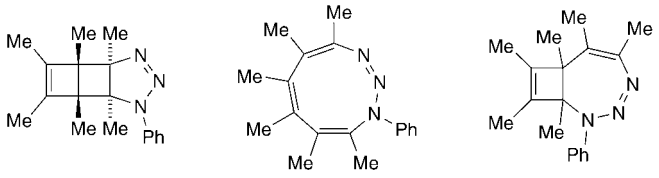
**Stephan Deuerlein** and **Dietmar Stalke***

Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg
(e-mail: dstalke@chemie.uni-wuerzburg.de)

Dedicated to Professor *Rolf Huisgen* on the occasion of his 85th birthday

The reactions of 1-azido-2,4,6-trimethyl- and 1-azido-2,6-dimethylbenzene with hexamethyl-*Dewar*-benzene (HMDB) give rise to the pentamethyl(iminoethyl)-4*H*-1,2-diazepines **4** and **5**, respectively. The X-ray crystal-structure analysis of **5** unequivocally established these unexpected structures, which motivated us to re-investigate the thermolysis of the adduct **1a** of HMDB and azidobenzene. Previously, the triazonine **2** was reported to be the major product, but this interpretation could not be corroborated now, and, instead, the 1-aminopyrrole **6** was identified as the true compound. The structure of the analogous compound **7**, obtained by thermolysis of the (1-azido-4-nitrobenzene)-HMDB adduct **1b**, was confirmed by X-ray diffraction. In the original literature investigation, a second product had been isolated, in addition to the alleged **2**, by chromatographic purificiation of the thermolysis mixture, and structure **3** had been ascribed to it. It turns out now that this compound is not a valence isomer of the major product, but a hydrolysis product, *i.e.*, the ketone **8**. The formation of the rather different compounds **4** and **5** on the one hand, and **6** and **7** on the other hand, can be rationalized straightforwardly by a sequence of pericyclic reactions leading to 3*H*-1,2-diazepines **11** as common intermediates, which are converted to either **4** and **5**, or **6** and **7**, depending on the nature of the aromatic group.

**Introduction.** – In 1972, *Paquette et al.* [1] reported the formation of triazolines upon reaction of four organic azides with hexamethyl-*Dewar*-benzene (=1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexa-2,5-diene; HMDB), *inter alia*, the product **1a** of azidobenzene (*Fig. 1*). Subsequently, *Paquette* and *Haluska* [2] subjected **1a** to thermolysis, and




**1a** **2** **3**

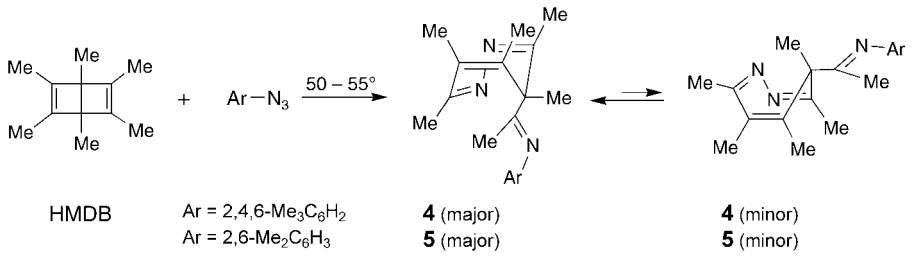
Fig. 1. *Structure of the cycloadduct* **1a** *of azidobenzene and hexamethyl*-Dewar-*benzene* (HMDB), *and the alleged structures of its major thermolysis product* (**2**) *and of a minor product* (**3**) *formed upon chromatographic purification* [2]

assigned the 1*H*-1,2,3-triazonine structure **2** to the major product. They postulated the formation of a second product that could not be observed, but was thought to be converted into the cyclobutatriazepine **3** on chromatography ($Al_2O_3$, activity III, or *Florisil*) of the pyrolysate. Heating of **3**, as well as treatment with *N*-phenyl-1,2,4-triazoline-3,5-dione, were described to result in the valence isomer **2**. A third thermolysis product of **1a** was characterized as 1,2,3,4,5,6-hexamethyl-7-phenyl-7-azanorbornadiene.

Encouraged by these studies, we prepared three cycloadducts of aromatic nitrile *N*-oxides with HMDB, which were shown to have a structure entirely analogous to that of **1a** [3]. Heating at 200° of the isoxazolines bearing a phenyl or a 4-nitrophenyl substituent led to the unspectacular result of the production of hexamethylbenzene. However, the 2,4,6-trimethylphenyl-substituted isoxazoline rearranged at a temperature as low as 130°, and gave rise to a benzisoxazole and an oxazonine derivative, in each of which a Me group of the starting compound had turned into a $CH_2$ group [3]. This astounding influence of a 2,4,6-trimethylphenyl as compared to a phenyl group motivated us to react 1-azido-2,4,6-trimethylbenzene with HMDB.

**Results.** – At first, we noticed that the process is slower than in the case of azidobenzene, with virtually no conversion occurring in a neat mixture of HMDB and 1-azido-2,4,6-trimethylbenzene at room temperature (*Scheme 1*). On heating at 80°, such a mixture produced only intractable material. However, the slow build-up of the concentration of a single product was observed by recording NMR spectra once and a while, when the mixture was kept at 50–55°. After four months, this concentration did not seem to increase anymore. Workup by chromatography (neutral $Al_2O_3$, activity I) provided a 32% yield of a 1:1 adduct of the reactants.

*Scheme 1*




As the NMR spectra clearly revealed, the product was neither a triazoline of type **1a** nor a triazonine of type **2**. Since there was no clue as to a certain structure, we tried to perform an X-ray crystal-structure analysis, but the insufficient quality of the crystals prevented the necessary refinement. Fortunately, we had carried out the reaction between 1-azido-2,6-dimethylbenzene and HMDB parallel to that of 1-azido-2,4,6-trimethylbenzene. The NMR spectra indicated products of the same kind for both azide additions, and the X-ray crystal-structure determination proceeded successfully in case of the 2,6-dimethylphenyl compound. The result is shown in *Fig. 2*. Thus, the products of the reactions between HMDB and 1-azido-2,4,6-trimethyl- and 1-azido-2,6-dimethylbenzene are the (arylimino)ethyldiazepines **4** and **5**, respectively (*Scheme 1*).

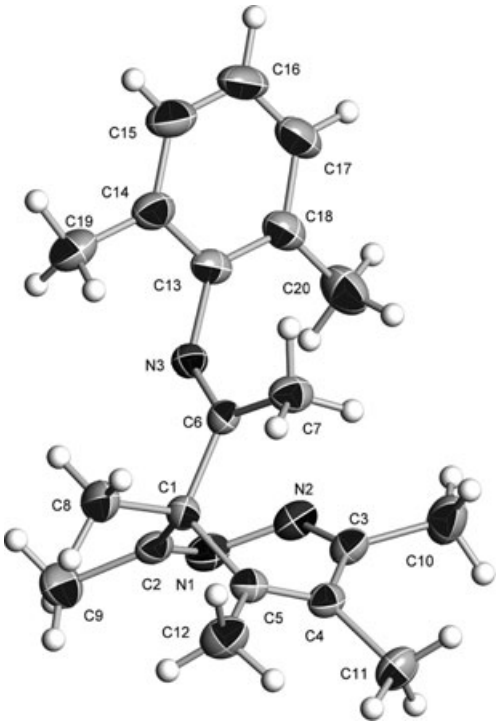



Fig. 2. *X-Ray crystal structure of* **5**. Anisotropic displacement parameters are depicted at the 50% probability level.

Specifically, compounds **4** and **5** are 4*H*-1,2-diazepine derivatives, a small class of compounds, which has been reviewed comprehensively [4].

The low-field $^1$H- (60 MHz) and $^{13}$C-NMR spectra (23 MHz) gave no indication of a special behavior of **4** and **5**. However, several broad signals in the high-field spectra (400/101 and 600/151 MHz, resp.) suggested the occurrence of a dynamic process. To get more information, we recorded the spectra of **4** (600/151 MHz) at $-65°$, and observed two sets of signals with an intensity ratio of 6 : 1. At higher temperatures, the signal pairs coalesced one by one, resulting in one signal set at 26°, with several absorptions still broadened. Free activation enthalpies of 13 – 14 kcal/mol of **4** (major product) were estimated [5] from the coalescence temperatures of $-30$ to $+26°$.

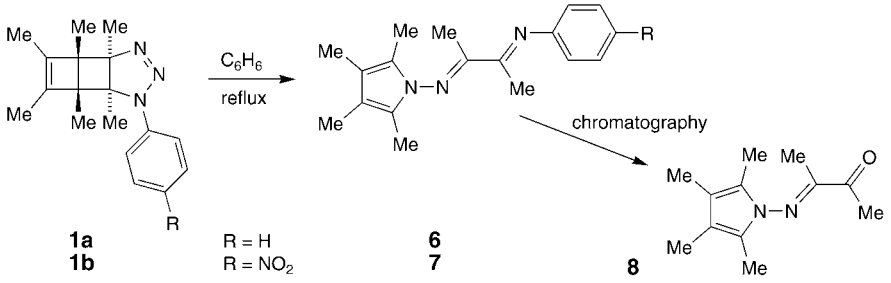
There are three possibilities for conformational motions in **4** and **5**, namely the rotation about the C–N single bond of the arylimine functionality, the (*E*/*Z*)-isomerization of the same group, and the inversion of the seven-membered ring. Rotation about the C–N single bond can safely be excluded, since this process cannot be the source of a second species, and is still frozen at 26°, as clearly demonstrated by three sharp Me signals of the aryl group in the $^1$H- and $^{13}$C-NMR spectra. From literature values of barriers to (*E*/*Z*)-isomerization or topomerization of imines (*e.g.*, 20.3 kcal/mol for acetone *N*-phenylimine [6]), we conclude on the basis of the observed barriers that the motion in **4** and **5** is considerably faster. Thus, we expect the inversion

of the diazepine system to be the origin of the equilibration of the two species. Indeed, such a conformational process has been described in the case of 3,5,7-triaryl-4*H*-1,2-diazepines, where two species of the same energy are separated by a free activation enthalpy of 18 kcal/mol at 70° [7]. Based on the observation that the aryliminoethyl group occupies the axial position in the crystal of **5** (*Fig. 2*), we assume that this arrangement for the major species of **4** and **5** applies in solution as well (*Scheme 1*).

In view of the surprising results of the reactions between HMDB and either 1-azido-2,4,6-trimethyl- or 1-azido-2,6-dimethylbenzene, we repeated the preparation [1] and the thermolysis of **1a** [2]. At variance with the previous conditions (heating at reflux in hexane) [1], we kept an equimolar mixture of azidobenzene and HMDB at room temperature, and isolated **1** in 59% yield after six weeks. Unlike *Paquette* and *Haluska* [2], who had thermolized **1** in refluxing decalin, we carried out the reaction at a much lower temperature. In a first experiment, the rearrangement was monitored in a solution of $C_6D_6$ by NMR spectroscopy. After immersion of an NMR tube with the sample in an oil bath of 82°, we observed a smooth progress of the reaction. Several intermediate products were observed, the isolation of which failed, however, and finally the compound was formed as the sole major product that *Paquette* and *Haluska* [2] had taken for the triazonine derivative **2**. None of the numerous further components amounted to more than 20% of the major product. From a preparative experiment in refluxing benzene, we isolated the major product by chromatography ($SiO_2$). It was identical in all respects with the compound of the alleged structure **2**.

However, the NMR spectra of this compound in $C_6D_6$ indicated only four types of Me groups, instead of six, as expected for **2**. Thus, the product possesses an element of twofold symmetry, which rules out structure **2**. *Paquette* and *Haluska* [2] had not recorded a $^{13}$C-NMR spectrum, and mistook the low number of signals in the $^1$H-NMR spectrum as an accidental coincidence. All of our data are in agreement with structure **6**, being a derivative of 1-amino-2,3,4,5-tetramethylpyrrole (*Scheme 2*).

*Scheme 2*




After elution of pure **6**, further fractions were obtained in the chromatographic workup of the crude thermolysis product. They contained still **6** and a compound with NMR signal patterns as those of **6**, but without absorptions of a phenyl group. When acidic $Al_2O_3$ (activity I) was used in the chromatographic separation, no pure **6** was eluted, but two fractions of similar quantities, with ratios of **6** and the second compound of 1:1 and 1:5, respectively. Based on the $^{13}$C-NMR signal at $\delta$(C) 198.9 and an IR band at 1703 cm$^{-1}$, we propose structure **8** for the second compound, which was

not present in the crude thermolysis product and, hence, had to be formed from **6** by hydrolysis during chromatography. This was corroborated by chromatography of pure **6** on *acidic* $Al_2O_3$ (activity III), which had been used for the isolation of the thermolysis products of **1a** previously [2]. In the order of elution with pentane/$Et_2O$ 15:1, we obtained unchanged **6**, **8**, and aniline.

The chromatographic behavior of **8** and the chemical shifts of its Me *singlets* in the $^1$H-NMR spectrum roughly agreed with the data given by *Paquette* and *Haluska* [2] for the alleged compound **3**. Since the authors described signals in their $^1$H-NMR spectrum that were not present in ours (*i.e.*, a Me *singlet* at $\delta$(H) 1.29 and *multiplets* of aromatic H-atoms), and because they did not mention the IR absorption at 1703 cm$^{-1}$, we think that they did not have a pure substance in their hands, but a mixture of **8**, **6**, and aniline. Such a mixture would rationalize the re-formation of **6**, the alleged **2**, by condensation of **8** and aniline on heating.

Chemical evidence for the structures **6** and **8** was provided by treatment of a mixture of them with 2 equiv. of 2,4-dinitrophenylhydrazine under standard conditions (EtOH, $H_2O$, $H_2SO_4$). The formation of diacetyl bis(2,4-dinitrophenylhydrazone) was corroborated by elemental analysis and comparison of its IR spectrum with that of an authentic sample. Aniline and 1-amino-2,3,4,5-tetramethylpyrrole were suspected in the mother liquor, which was, thus, neutralized with NaOH, and then subjected to steam distillation. The organic material isolated from the receiver was shown by NMR spectroscopy to unambiguously contain aniline, whereas 1-amino-2,3,4,5-tetramethylpyrrole could not be identified beyond doubt, although being a known compound [8], due to the presence of considerably more Me *singlets* than expected. Probably, most, if not all, of the pyrrole was decomposed under the strongly acidic conditions of the reaction.

In order to create a second example for the type of the rearrangement **1a** → **6**, we prepared the triazoline **1b** from HMDB and 1-azido-4-nitrobenzene (*Scheme 2*). The cycloaddition proceeded somewhat faster than that of azidobenzene, and afforded **1b** in 60% yield. Its thermolysis in refluxing benzene gave rise to a 34% yield of a product, the analytical data of which were entirely analogous to those of **6**. An X-ray diffraction analysis confirmed the structure **7** (*Fig. 3*). As anticipated, chromatography on acidic $Al_2O_3$ (activity III) brought about the partial hydrolysis of **7**, affording **8** and 4-nitroaniline, in addition to unchanged **7**.

**Discussion.** – Even though structurally very different, the products **4** and **5** on the one hand, and **6** and **7** on the other hand, bear a common feature, namely the separation of the three-N-atom subunit of the azide, added onto HMDB, into a hydrazine and an imine functionality. This is why we propose that the first steps of the rearrangements are the same for both types of products, and that the 1,3-dipolar cycloaddition to generate a triazoline **1** is the initial reaction in the case of 1-azido-2,4,6-trimethyl- and 1-azido-2,6-dimethylbenzene as well, although the corresponding triazolines could not be observed. Obviously, these sterically demanding aryl groups retard the cycloaddition to a rate that is slower than that of the transformation of the resulting triazoline.

Since the 1,3-dipolar cycloreversion of $\Delta^2$-triazolines to a diazomethane and an imine entity is well known [9], in particular when a small ring is annulated to the C–C subunit [10], we think that the decomposition of **1** starts with the cleavage of the five-

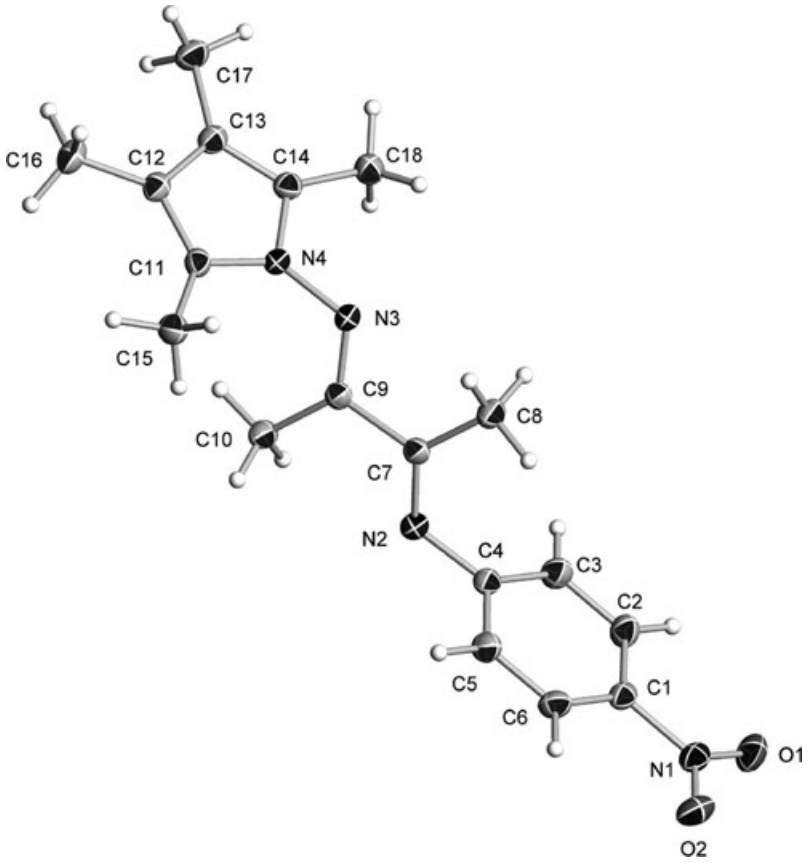
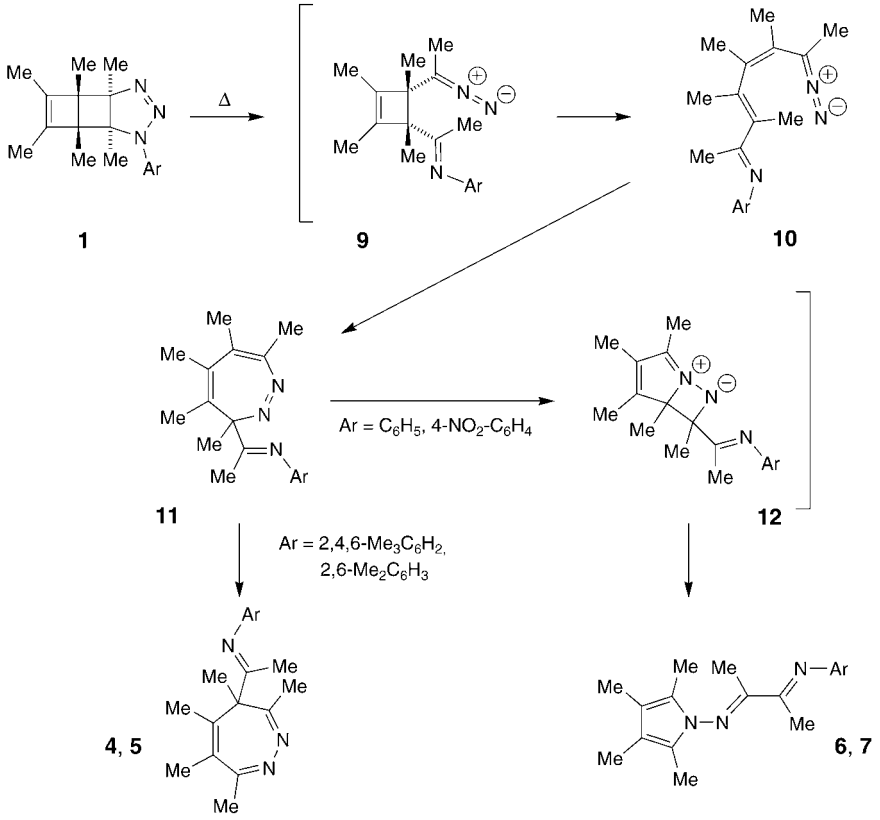



Fig. 3. *X-Ray crystal structure of* **7**. Anisotropic displacement parameters are depicted at the 50% probability level.

membered ring to generate the imino functionalized diazoalkane **9** (*Scheme 3*). In addition to the weakness of the N–N bond, the strain energy of the cyclobutane subunit provides the driving force for this process. The electrocyclic ring opening of cyclobutenes belongs to the classical pericyclic reactions. It proceeds particularly fast when functional groups occupy positions 3 and 4 [11]. Thus, the $\alpha,\beta,\gamma,\delta$-unsaturated diazoalkane **10** should emerge from **9**. The 1,7-electrocyclization of such diazoalkanes to 3*H*-diazepines has precedent [12], which is why we propose the conversion of **10** into **11**. This diazepine is considered to be the point of bifurcation of the pathway, since the 1,5-migration of the iminoacetyl group leads to the 4*H*-1,2-diazepines **4** and **5**, whereas an allyl rearrangement with ring contraction gives rise to **6** and **7**. It is astounding that a substituent, positioned as remote as anticipated from formula **11**, has such a dramatic influence on the course of the reaction. However, the molecular shape of **5** in the crystal (*Fig. 2*) demonstrates that the imino group may well reside close to the center of **11**. With respect to the ring contraction of **11** *en route* to **6** and **7**, a stepwise process *via* the 1,3-dipole **12** is deemed possible.

Scheme 3. *Mechanistic Proposal for the Rearrangement of Triazolines* **1** *to the Diazepines* **4** *and* **5**, *and the Pyrroles* **6** *and* **7**




**Conclusions.** – To satisfy our curiosity about the influence of a 2,4,6-trimethylphenyl group in comparison to a phenyl group, we treated hexamethyl-*Dewar*-benzene (HMDB) with 1-azido-2,4,6-trimethylbenzene. Although azidobenzene smoothly furnishes the phenyltriazoline **1a**, its analogue with a 2,4,6-trimethylphenyl instead of a phenyl group could not be observed. Rather, the 4*H*-1,2-diazepine derivative **4** was isolated. This unanticipated finding caused a re-investigation of the thermolysis of **1a**, with the result that the structure of the major product, previously assumed to be the triazonine **2**, must be revised. This compound actually is the derivative **6** of 1-amino-2,3,4,5-tetramethylpyrrole. Being an imine, **6** undergoes partial hydrolysis upon chromatographic separation to afford the ketone **8**, which was previously mistaken as the cyclobutatriazepine **3**. In summary, the addition reaction between aromatic azides and HMDB leads (or is believed to lead) to the expected triazolines, the thermolysis of which gives rise to surprising products, whose formation can be rationalized by sequences of pericyclic reactions. Thus, another interesting aspect is added to the rich chemistry of HMDB [13].

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## Experimental Part

*General*. The aromatic azides, except 1-azido-2,6-dimethylbenzene, were prepared according to [14]. Flash chromatography (FC): $SiO_2$ (0.063 – 0.032 μm) and $Al_2O_3$ (activities I or III). Solvents were of commercial grade an neither dried nor distilled. M.p.: *Kofler* hot stage from *C. Reichert, Optische Werke AG*, Vienna, Austria. IR Spectra: *JASCO FT/IR-410*; selected absorption bands in $cm^{-1}$. NMR Spectra: *Bruker HX 90*, *Avance 400*, and *DMX 600*; chemical shifts $\delta$ in ppm rel. to $Me_4Si$ (= 0 ppm) by using solvent signals as internal reference ($CDCl_3$: $\delta$(H) 7.26, $\delta$(C) 77.0; $C_6D_6$: $\delta$(H) 7.16), coupling constants *J* in Hz. EI-MS (70 eV): *Finnigan MAT 8200*, in *m/z* (rel. %). Elemental analyses: *LECO CHNS-932* elemental analyzer.

*3,4,5,6,7-Pentamethyl-4-{1-[(2,4,6-trimethylphenyl)imino]ethyl}-4*H*-1,2-diazepine* (**4**). 1-Azido-2,4,6-trimethylbenzene (536 mg, 3.32 mmol) and HMDB (518 mg, 3.19 mmol) were mixed in a small round-bottomed flask. The air above the mixture was then replaced by $N_2$. The flask was closed, and kept at 50 – 55° in an oven. Although the mixture turned black within several days, an NMR spectrum of a sample indicated that, at best, very little conversion had occurred. However, after several weeks, the formation of a single product was discernible in a considerable concentration rel. to that of a number of minor components. After 4 months, the concentration of the major product did no longer increase. Purification by FC (neutral $Al_2O_3$, activity I; pentane/$Et_2O$ 1:2) afforded **4** (330 mg, 32%). Colorless solid. M.p. 140 – 142°. IR (KBr): 2900*s*, 1650*s*, 1465*s*, 1435*s*, 1370*s*, 1355*s*, 1295*m*, 1245*m*, 1240*m*, 1220*m*, 1205*m*, 1150*w*, 1085*s*, 1075*m*, 995*m*, 930*m*, 860*m*, 850*m*, 780*m*, 710*w*. $^1$H-NMR (600 MHz, $CDCl_3$)[2]): 1.28 (br. *s*, 3 H) [1.22, 1.51; 10°]; 1.77 (*s*, 3 H) [1.78, 1.73; −10°]; 1.89 (*s*, Ar−*Me*) [1.89, 1.82; −10°]; 1.91 (*s*, 3 H) [1.89, 1.91; −30°]; 1.96 (*s*, 3 H) [1.93, 1.89; −10°]; 2.00 (*s*, Ar−*Me*) [2.01, 2.06; −10°]; 2.178 (*s*, 3 H) [2.17, 2.14; −10°]; 2.183 (*s*, 3 H) [2.18, 2.16; −30°]; 2.187 (*s*, Ar−*Me*) [2.20, 2.23; −10°]; 6.71 (*s*, 1 H) [6.72, 6.72]; 6.74 (*s*, 1 H) [6.74, 6.72; −30°]. $^{13}$C-NMR (151 MHz, $CDCl_3$)[2]): 16.4 [16.4, 16.75; −10°]; 16.4 (very br.) [15.9, 19.5; 26°]; 16.8 (br.) [16.82, 18.1; 10°]; 18.57 (Ar−*Me*) [18.9, 18.5; 0°]; 18.63 (Ar−*Me*) [18.6, 19.2; 0°]; 20.5 (Ar−*Me*) [20.6, 20.5; −30°]; 21.6 [22.0, 21.8; −10°]; 23.8 (br.) [23.7, 25.8; 15°]; 24.1 [23.7, 23.9; −10°]; 58.1 [57.4, 58.1; −5°]; 125.1 [125.4, 125.5; −10°]; 125.7 (br.) [125.6, 124.8; 10°]; 126.4 [126.3, 126.1; −10°]; 128.3 (CH) [127.9, 128.1; −10°]; 128.6 (CH) [128.2, 128.2]; 131.7 [131.7, 131.9; −10°]; 140.3 (very br.) [139.7, 143.0; 20°]; 145.4 [144.8, 144.7; −10°]; 153.3 (br.) [154.1, 153.3; −5°]; 155.2 (very br.) [155.6, 160.2; 26°]; 171.4 (very br.) [171.3, 175.0; 26°]. EI-MS: 323 (1, $M^+$), 241 (18), 161 (12), 160 (100, $ArNCMe^+$), 145 (20), 123 (15), 119 (18), 91 (17), 41 (10). Anal. calc. for $C_{21}H_{29}N_3$ (323.48): C 77.97, H 9.04, N 12.99; found C 78.06, H 8.91, N 12.80.

*3,4,5,6,7-Pentamethyl-4-{1-[(2,6-dimethylphenyl)imino]ethyl}-4*H*-1,2-diazepine* (**5**). Prepared from 1-azido-2,6-dimethylbenzene according to the procedure described for **4**. Pure **5** was obtained by FC (neutral $Al_2O_3$, activity I; pentane/$Et_2O$ 2:3) in 33% yield. Colorless solid. M.p. 117 – 119°. IR (KBr): 3010*w*, 2981*w*, 2946*m*, 2914*m*, 1651v*s*, 1593*m*, 1464*s*, 1437*s*, 1380*m*, 1365*m*, 1357*m*, 1294*w*, 1250w, 1201*s*, 1090*s*, 1072*m*, 996*w*, 930*w*, 809*w*, 775w, 765*m*. $^1$H-NMR (400 MHz, $CDCl_3$, 27°): 1.30 (br. *s*, 3 H); 1.79 (*s*, 3 H); 1.92 (*s*, 3 H); 1.94 (*s*, 3 H); 1.97 (*s*, 3 H); 2.04 (*s*, 3 H); 2.19 (*s*, 3 H); 2.20 (*s*, 3 H); 6.81 (*t*, *J* = 7.5, 1 H); 6.90 (*d*, *J* = 7.5, 1 H); 6.93 (*d*, *J* = 7.5, 1 H). $^{13}$C-NMR (101 MHz, $CDCl_3$, 27°)[3]): 16.5; 16.6 (very br.); 16.8 (br.); 18.7; 18.8; 21.7; 24.0 (br.); 24.2; 58.1; 122.8 (CH); 125.5; 125.9; 126.7; 127.7 (CH); 128.0 (CH); 140.3 (very br.); 148.0; 153.3; 155.9 (very br.); 171.3 (very br.). EI-MS: 309 (2, $M^+$), 227 (21), 212 (10), 147 (12), 146 (100, $ArNCMe^+$), 131 (16), 123 (17), 105 (27), 103 (11), 79 (21), 77 (17). Anal. calc. for $C_{20}H_{27}N_3$ (309.45): C 77.63, H 8.79, N 13.58; found: C 77.35, H 8.85, N 13.53.

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1) See H. Quast, M. Ach, J. Balthasar, T. Hergenröther, D. Regnat, J. Lehmann, K. Banert, *Helv. Chim. Acta* **2005**, *88*, 1589.

2) NMR Spectra were recorded at 26, −10, −30, and −65°. At −65°, two sets of signals were observed, with an intensity ratio of 6:1, which coalesced at higher temp., and resulted in one set of signals at 26°, at which temp. several signals were still broadened. The date given here are the chemical shifts at 26° and, in square brackets, the chemical shifts of the major and the minor component at −65°, as well as the approximate coalescence temp. As far as specified, assignments are based on NOESY ($^1$H) or HSQC ($^{13}$C) spectra.

3) As far as specified, assignments are based on a DEPT spectrum.

*(1α,2β,5β,6α)-1,2,3,4,5,6-Hexamethyl-9-phenyl-7,8,9-triazatricyclo[4.3.0.0$^{2,5}$]nona-3,7-diene* (**1a**). Azidobenzene (6.37 g, 53.5 mmol) and HMDB (8.67 g, 53.4 mmol) were mixed in a small flask under $N_2$, and kept at r.t. in the dark for six weeks. The progress of the reaction was monitored by recording an NMR spectrum of a small sample once and a while. Crystals were formed on treatment of the mixture with a spatula. They were washed with cold pentane to give pure **1a** (8.86 g, 59%; lit. 65.5% [1]). The published $^1$H-NMR spectrum of **1a** was not as well-resolved as ours, and the corresponding $^{13}$C-NMR data are reported here for the first time. $^1$H-NMR (400 MHz, $CDCl_3$): 0.94 (*s*, 3 H); 0.96 (*s*, 3 H); 1.24 (*s*, 3 H); 1.26 (*s*, 3 H); 1.71 (*q*, *J* = 1.1, 3 H); 1.72 (*q*, *J* = 1.1, 3 H); 7.03 (*tt*, arom. H); 7.25–7.35 (*m*, 4 arom. H). $^{13}$C-NMR (23 MHz, $CDCl_3$): 8.4; 10.3 (double intensity); 11.0; 15.5; 16.6; 57.2; 57.7; 66.5; 90.3; 116.6 (2 arom. *o*-C); 122.0 (arom. *p*-C); 128.3 (2 arom. *m*-C); 140.2; 141.3; 142.7.

*2,3,4,5-Tetramethyl*-N-*[1-methyl-2-(phenylimino)propylidene]-1*H-*pyrrol-1-amine* (**6**) *and 3-[(2,3,4,5-Tetramethyl-1*H-*pyrrol-1-yl)imino]butan-2-one* (**8**). A soln. of **1a** (3.62 g, 12.9 mmol) in anh. benzene (11 ml) was heated at reflux under $N_2$ for 5 d. Then, the mixture was subjected to FC ($SiO_2$; pentane/$Et_2O$ 15 : 1) to afford, in this order, *1*) a mixture of **6** with unidentified impurities (162 mg), *2*) crystals of pure **6** (276 mg, 8%) identical in all respects with the alleged **2** [2], *3*) crystals of a 7 : 1 mixture of **6** and **8** (528 mg, 15%), and *4*) an oily 3 : 2 mixture of **6** and **8** (155 mg, 5%). When acidic $Al_2O_3$ (activity I) was used in the FC, no pure **6** was obtained, but two fractions of approximately the same quantity eluted, with **6**/**8** ratios of 1 : 1 and 1 : 5. FC of pure **6** on acidic $Al_2O_3$ (activity III; pentane/$Et_2O$ 15 : 1) furnished, in this order, unchanged **6**, rather pure **8**, and aniline. The identity of the latter was established by comparison of its $^1$H-NMR spectrum with that of an authentic sample. The reported $^1$H-NMR spectrum of **6** [2] was not as well-resolved as ours.

*Data of* **6**. $^1$H-NMR (400 MHz, $CDCl_3$)[4]): 1.99 (*s*, 12 H) [1.96 (*s*, 6 H), 2.08 (*s*, 6 H)]; 2.17 [2.09] (*s*, 3 H); 2.19 [2.11] (*s*, 3 H); 6.80 [6.68] (*m*, 2 arom. *o*-H); 7.13 [6.94] (*tt*, arom. *p*-H); 7.37 [ *ca.* 7.16] (*m*, 2 arom. *m*-H). $^{13}$C-NMR (101 MHz, $CDCl_3$): 9.3 (2 C); 9.8 (2 C); 15.0; 15.9; 112.7 (2 C); 118.8 (2 arom. *o*-C); 119.7 (2 C); 124.1 (arom. *p*-C); 129.0 (2 arom. *m*-C); 150.4; 166.7; 174.3.

*Data of* **8**. IR (film): 2964*m*, 2919*s*, 2861*m*, 1703v*s*, 1440*m*, 1425*m*, 1361*s*, 1329*m*, 1278*s*, 1123*m*. $^1$H-NMR (400 MHz, $CDCl_3$)[4]): 1.95 [1.79] (*s*, 6 H); 1.96 [2.00] (*s*, 6 H); 2.01 [1.72] (*s*, 3 H); 2.55 [2.27] (*s*, 3 H). $^{13}$C-NMR (101 MHz, $CDCl_3$): 9.2 (2 C); 9.9 (2 C); 14.2; 25.4; 114.0 (2 C); 120.3 (2 C); 168.6; 198.9. EI-MS: 206 (12, $M^+$), 123 (7), 122 (13), 79 (6), 43 (100), 42 (6), 41 (5). HR-EI-MS: 206.1431 ($M^+$, $C_{12}H_{18}N_2O^+$; calc. 206.1436).

*(1α,2β,5β,6α)-1,2,3,4,5,6-Hexamethyl-9-(4-nitrophenyl)-7,8,9-triazatricyclo[4.3.0.0$^{2,5}$]nona-3,7-diene* (**1b**). A soln. of 1-azido-4-nitrobenzene (1.01 g, 6.15 mmol) and HMDB (1.02 g, 6.29 mmol) in anh. benzene (5 ml) was kept under $N_2$ in the dark at r.t. for 3 weeks, during which time yellow needles precipitated. They were collected by suction filtration, washed with cold pentane, and dried to give **1b** (1.21 g, 60%). An anal. sample was recrystallized from MeOH/$CH_2Cl_2$. M.p. 164–166° (MeOH/$CH_2Cl_2$). $^1$H-NMR (400 MHz, $CDCl_3$): 0.87 (*s*, 3 H); 0.94 (*s*, 3 H); 1.31 (*s*, 3 H); 1.34 (*s*, 3 H); 1.71 (*dq*, *J* = 1.1, 3 H); 1.74 (*dq*, *J* = 1.1, 3 H); 7.37 (*m*, 2 H); 8.19 (*m*, 2 H). $^{13}$C-NMR (101 MHz, $CDCl_3$): 8.7; 10.71; 10.74; 11.3; 16.0; 16.6; 57.8; 57.9; 65.9; 92.9; 115.0 (2 CH); 125.3 (2 CH); 141.7; 141.8; 143.3; 145.9. EI-MS: 326 (0.1, $M^+$), 244 (15), 243 (8), 164 (11), 163 (100), 117 (45), 108 (9), 76 (18). Anal. calc. for $C_{18}H_{22}N_4O_2$ (326.40): C 66.24, H 6.79, N 17.17; found: C 65.93, H 6.70, N 17.46.

*2,3,4,5-Tetramethyl*-N-*[1-methyl-2-[(4-nitrophenyl)imino]propylidene]-1*H-*pyrrol-1-amine* (**7**). A soln. of **1b** (1.21 g, 3.71 mmol) in anh. benzene (8 ml) was heated at reflux under $N_2$ for 5 d. Then, the mixture was subjected to FC ($SiO_2$; pentane/$Et_2O$ 8 : 1) to give **7** (411 mg, 34%). When pure **7** (124 mg) was subjected to FC on acidic $Al_2O_3$ (activity III), three fractions were obtained, in the following order, on elution with light petroleum ether/$Et_2O$ 15 : 1: **8** (10 mg), **7** (68 mg), and a mixture (80 mg) containing 4-nitroaniline and unidentified components. 4-Nitroaniline was identified by comparison of its $^1$H-NMR spectrum with that of an authentic sample.

*Data of* **7**. Orange crystals. M.p. 168–172° ($CH_2Cl_2$). $^1$H-NMR (250 MHz, $CDCl_3$): 1.99 (*s*, 6 H); 2.00 (*s*, 6 H); 2.19 (*s*, 3 H); 2.21 (*s*, 3 H); 6.92 (*m*, 2 H); 8.29 (*m*, 2 H). $^{13}$C-NMR (63 MHz, $CDCl_3$): 9.3 (2 C); 9.8 (2 C); 15.1; 16.4; 113.2 (2 C); 119.0 (2 CH); 120.0 (2 C); 125.1 (2 CH); 144.2; 156.3; 167.8; 172.4. EI-MS: 326 (47, $M^+$), 189 (45), 188 (30), 174 (20), 164 (17), 163 (100), 123 (20), 122 (88), 121 (41), 117 (82), 76 (38). Anal. calc. for $C_{18}H_{22}N_4O_2$ (326.40): C 66.24, H 6.79, N 17.17; found: C 65.79, H 6.87, N 16.97.

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[4]) Values in brackets refer to $C_6D_6$ soln.

*X-Ray Crystal-Structure Determinations*[5]). Crystals of **5** and **7** were grown from $Et_2O$. Intensity data were collected on a *Bruker Smart APEX CCD* diffractometer, with a low-temp. $N_2$ gas-stream device [15] at 173 K (**5**) and 100 K (**7**). Monochromated Mo$K_\alpha$ radiation ($\lambda = 71.073$ pm) and an $\omega$-scan mode ($\Delta\omega = -0.3°$) at fixed $\varphi$-angles were used, with a detector-to-sample distance of 5 (**5**) and 6 cm (**7**), and exposure times of 30 (**5**) and 10 s (**7**), resp. For **5**, out of 19171 collected reflections, of which 3202 were independent, 2922 with $I > 2\sigma(I)$ were used for structure determination. In the case of **7**, 3061 reflections with $I > 2\sigma(I)$ out of 3496 unique reflections (36910 collected in total) were used for the same purpose. For both structure determinations, the program SMART was used for data collection, SAINT for data integration, SADABS [16] for empirical absorption corrections, and XPREP for merging the data. The structures were solved [17] by direct methods, and refined against $F^2$ using the SHELXL-97 package [18]. All non-H-atoms were refined anisotropically, and a riding model was employed in the refinement of the H-atom positions.

*Crystal Data of* **5**. $C_{20}H_{27}N_3$; $M_r$ 309.45 g/mol; crystal dimensions: $2.5 \times 0.5 \times 0.5$ mm; $Z = 4$; $\varrho_{calc} = 1.141$ Mg/m$^3$; space group $P2_1/c$ (monoclinic), with $a = 1714.0(3)$, $b = 727.11(12)$, and $c = 1610.5(3)$ pm, $\beta = 116.156(4)°$; $V = 1.8017(5)$ nm$^3$, $\mu = 0.068$ mm$^{-1}$; $\theta_{max} = 25.07°$, max/min transmission = 0.76; 219 parameters; $R1 = 0.0727$ [$I > 2\sigma(I)$], $wR2 = 0.1407$ (all data); goodness-of-fit = 1.237, max/min residual electron density = 0.214/ − 0.191 e/Å$^3$.

*Crystal Data of* **7**. $C_{18}H_{22}N_4O_2$; $M_r = 326.40$ g/mol; crystal dimensions $4.0 \times 3.0 \times 2.0$ mm; $Z = 8$; $\varrho_{calc} = 1.269$ Mg/m$^3$; space group *Pbca* (orthorhombic), with $a = 1530.12(10)$, $b = 1443.27(9)$, and $c = 1546.83(10)$ pm; $V = 3.4160(4)$ nm$^3$; $\mu = 0.085$ mm$^{-1}$; $\theta_{max} = 26.38°$, max/min transmission = 0.91; 223 parameters; $R1 = 0.0404$ [$I > 2\sigma(I)$], $wR2 = 0.1092$ (all data); goodness-of-fit = 1.032; max/min residual electron density = 0.351/ − 0.177 e/Å$^3$.

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[5]) The crystallographic data (excluding structure factors) for **5** and **7** have been deposited with the *Cambridge Crystallographic Data Centre* (CCDC) as supplementary publication numbers CCDC-263631 and -263632, resp. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail:data_request@ccdc.cam.ac.uk; internet: http://www.ccdc.cam.ac.uk/data_request/cif).

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